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Review article

An overview of the behaviour of biomass during combustion: Part II. Ash fusion and ash formation mechanisms of biomass types

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ABSTRACT

An extended overview of the phase–mineral transformations of organic and inorganic matter during biomass combustion was conducted in Part I of the present work. The ash fusion and ash formation mechanisms of biomass types and sub-types during combustion are described in the present Part II. For that purpose the identified systematic associations based on the occurrence, content and origin of elements and phases in the biomass ash (BA) system, namely (1) Si–Al–Fe–Na–Ti (mostly glass, silicates and oxyhydroxides); (2) Ca–Mg–Mn (commonly carbonates, oxyhydroxides, glass, silicates and some phosphates and sulphates); and (3) K–P–S–Cl (normally phosphates, sulphates, chlorides, glass and some silicates and carbonates); were used as classification of BAs into four types ("S", "C", "K" and "CK") and six sub-types with high, medium and low acid tendencies and their description was given. Then, topics related to ash fusion behaviour such as: some general considerations and observations about ash melting; ash fusion temperatures (AFTs) of biomass and their comparisons with coal; relationships between AFTs and inorganic composition of biomass and coal; and ash fusion mechanisms of biomass and coal are characterized. Further, issues connected with the ash formation mechanisms of BA types and sub-types are discussed. Subsequently, aspects related to potential applications of ash formation mechanisms for BA types and sub-types, namely some key technological problems (fusion, slagging and fouling predictions, low ash fusion temperatures, co-combustion and application of BA) and environmental risks (volatilization, capture and water leaching of hazardous elements) are described. Finally, it is emphasized that the application of this new classification approach based on combined phase–mineral and chemical composition of biomass and BA has not only fundamental importance, but also has potential applications in prediction of behaviour and properties connected with the innovative and sustainable utilization of biomass and BA. It is also demonstrated that the definitive utilization, technological and environmental advantages and challenges related to biomass and BA associate preferentially with their specific types and sub-types and they could be predictable to some extent by using the above or similar combined chemical and phase–mineral classification approaches.

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Nomenclature

A	ash yield	M	moisture
AFT	ash fusion temperature	MM	marine macroalgae
BA	biomass ash	MP	melting point
BC	beech wood chips	OM	organic matter
CC	corn cobs	PP	plum pits
daf	dry, ash-free basis	R^2	correlation coefficient
db	dry basis	RH	rice husks
DT	initial deformation temperature	SG	switchgrass
DTA	differential-thermal analysis	SS	sunflower shells
DWR	dry water-soluble residue	ST	spherical temperature
FC	fixed carbon	TGA	thermo-gravimetric analysis
FT	fluid temperature	VM	volatile matter
HAP	hazardous air pollutant elements	WS	walnut shells
HT	hemispherical temperature	XRD	X-ray powder diffraction
HTA	high-temperature ash (>500 °C)	%	weight %
IM	inorganic matter		

1. Introduction

Extensive reference peer-reviewed data plus own investigations for both biomass and biomass ash systems were used recently to perform several extended overviews related to: (1) chemical composition of biomass [1]; (2) organic and inorganic phase composition of biomass [2]; (3) phase–mineral and chemical composition of biomass ash (BA) [3]; and (4) potential utilization, technological and ecological advantages and challenges of BA [4]; respectively. New classifications based on data from proximate, ultimate, ash, structural and mineralogical analyses of biomass and BA have also been introduced therein [1–3].

The present work is an overview that contains two parts and describes the behaviour of biomass during combustion, namely: (1) phase–mineral transformations of organic matter (OM) and inorganic matter (IM); and (2) ash fusion and ash formation mechanisms, respectively. Part I [5] included major issues related to the composition, occurrence, transformation and origin of common constituents in biomass and BA such as: (1) OM, namely cellulose, hemicellulose, lignin, char and other organic phases plus organic minerals; and (2) IM such as silicates, oxides and hydroxides, phosphates, sulphates (plus sulphides, sulphosalts, sulphites and thiosulphates), carbonates (plus bicarbonates), chlorides (plus chlorites and chlorates), nitrates, glass, amorphous (non-glass) material and other inorganic phases; and they were described and compared to coal ash. A systematization of physico-chemical transformations during biomass combustion has also been given in Part I. This is the second part of the present overview and includes a critical review of publications and own investigations as an attempt will be undertaken to address the following objectives:

(1) Clarification of the ash fusion behaviour of biomass.
(2) Explanation of the ash formation mechanisms associated with biomass types and sub-types during combustion.
(3) Indication of some key technological and environmental challenges connected with combustion of biomass types and sub-types and application of their BAs.

2. Materials, methods and data used

The materials, methods and most of the data used were presented in Part I [5]. The data given in the former part include the chemical ash composition of biomass groups and sub-groups, the

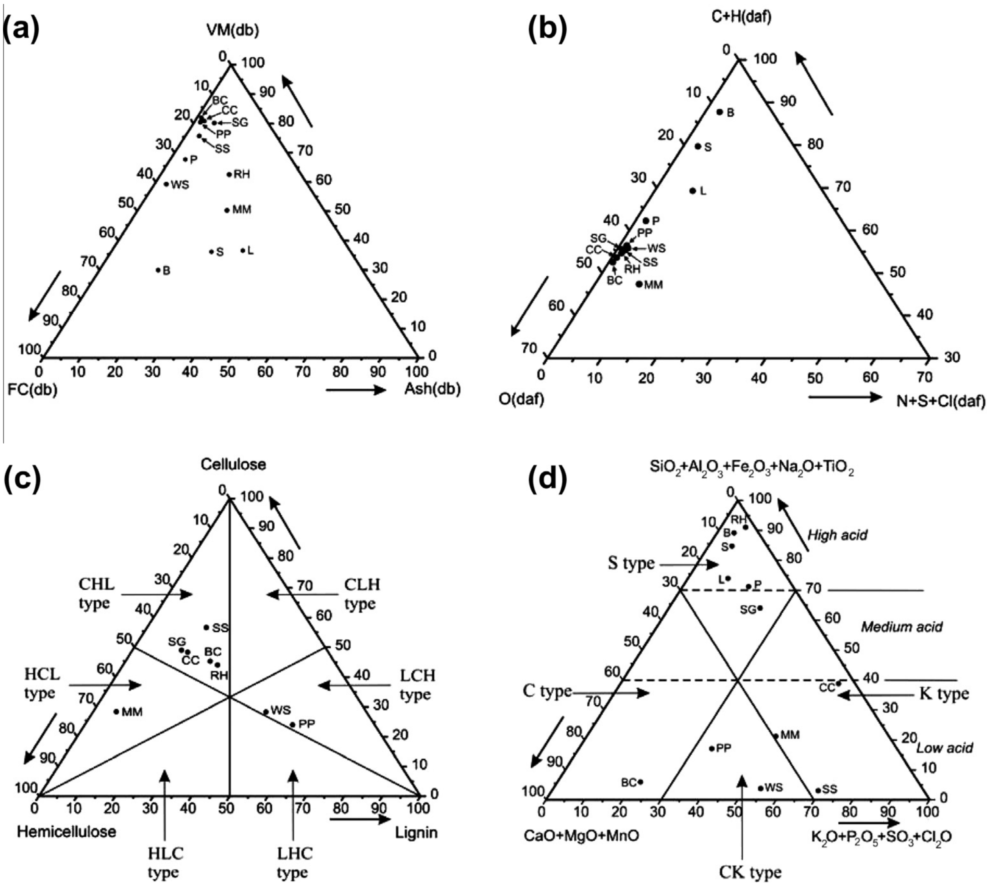

Fig. 1. Positions of eight biomass varieties in some classification systems based on data from: (a) proximate; (b) ultimate; (c) structural; and (d) ash analyses, wt.%. Abbreviations: B, bituminous coal; BC, beech wood chips; CC, corn cobs; daf, dry, ash-free basis; db, dry basis; FC, fixed carbon; L, lignite; MM, marine macroalgae; P, peat; PP, plum pits; RH, rice husks; S, sub-bituminous coal; SG, switchgrass; SS, sunflower shells; VM, volatile matter; WS, walnut shells.

phases and minerals identified or assumed in BA, the possible physico-chemical formations, transformations and reactions during biomass combustion and BA storage, as well as the melting point (MP) temperatures of many inorganic phases and minerals identified or assumed in biomass and BA. The results used in this Part II were obtained from: (1) reference peer-reviewed investigations; and (2) own new data and studies plus some novel interpretations of reference data. For better differentiation, they are referred to as: "reference investigations" and "present study" throughout the text, respectively.

Eight biomass samples were collected and studied for additional clarification of the chemical and phase composition of biomass and BA and behaviour of biomass during combustion in Part I [5], as well as ash fusion and ash formation mechanisms of biomass types in the present study. They include beech wood chips (BC), corn cobs (CC), marine macroalgae (MM), weathered plum pits (PP), rice husks (RH), switchgrass (SG), sunflower shells (SS) and walnut shells (WS) belonging to different biomass groups and sub-groups specified by origin (biodiversity and source) [1]. The majority of investigations up to now have been concentrated on woody biomass and wheat straw as solid biofuels. Most of the eight samples are herbaceous and agricultural residues and algae (sea lettuces) and much less is known about them. The selection of these samples is also based on their variable: (1) proximate (Fig. 1a), ultimate (Fig. 1b) and structural (Fig. 1c) composition; and especially (2) inorganic chemical composition (Tables 1 and 2, and Figs. 1d and 2). Another big advantage of these samples for comparative investigations is that they belong to: (1) different organic structural types ("CHL", "LCH" and "HCL" in Fig. 1c); (2) all inorganic chemical types ("S", "C", "K", and "CK" types in Fig. 1d) and different sub-types (Fig. 1d); and (3) all inorganic acid tendencies (high, medium and low in Fig. 1d); that have been specified recently for biomass and BA [1–3]. Additionally, five samples from them fit in the low acid "K" and "CK" types and sub-types (Fig. 1d), which are among the most problematic biomass resources from technological and environmental points of view [1–5]. Finally, the composition of these eight biomass samples differs widely in comparison with coals (Tables 1 and 2, and Figs. 1 and 2).

The biomass samples were investigated using methods such as light microscopy, powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), and differential-thermal (DTA), thermo-gravimetric (TGA) and chemical analyses, as well as some leaching, precipitation, ashing and other procedures described in detail in Part I [5]. Additionally, the common minerals in high-temperature ashes (HTAs) produced at 500, 700, 900, 1100, 1300 and 1500 °C were evaluated by using the data obtained by XRD patterns. For that purpose, semi-quantitative XRD determinations were performed by integral area and height measurements of the crystalline matter, amorphous halo and individual mineral peaks based on the relative intensities (counts per second) of XRD patterns as described in detail earlier for coal ash [6]. Shortly, the areas of subtracted amorphous halo (in the interval 10–50° 2θ for Cu Kα radiation) and crystalline matter (all peak areas of the minerals in the interval 10–70° 2θ for Cu Kα radiation) were measured. The results were normalized to 100% and reported as weight % of the inorganic amorphous material (IAM) and inorganic crystalline

Table 1
Chemical ash composition of biomass groups and sub-groups (86 varieties of biomass) plus algae and four solid fossil fuel types based on high-temperature ash analyses (normalized to 100%), wt.% (based on [1,3]). The Mn contents are additionally given.

Biomass group and sub-group	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	Sum	Mn	Samples
1. Wood and woody biomass (WWB)													
Mean	22.22	43.03	10.75	3.48	5.09	6.07	3.44	2.78	2.85	0.29	100.00	1.32	28
Minimum	1.86	5.79	2.19	0.66	0.12	1.10	0.37	0.36	0.22	0.06		0.08	28
Maximum	68.18	83.46	31.99	13.01	15.12	14.57	9.54	11.66	29.82	1.20		3.57	28
2. Herbaceous and agricultural biomass (HAB)													
Mean	33.39	14.86	26.65	6.48	3.66	5.62	3.26	3.61	2.29	0.18	100.00	0.13	44
Minimum	2.01	0.97	2.29	0.54	0.10	0.19	0.22	0.01	0.09	0.01		0.02	44
Maximum	94.48	44.32	63.90	31.06	14.60	16.21	36.27	14.74	26.20	2.02		0.46	44
2.1. Grasses (HAG)													
Mean	46.18	11.23	24.59	6.62	1.39	4.02	0.98	3.66	1.25	0.08	100.00	0.31	10
Minimum	8.73	2.98	2.93	3.14	0.67	1.42	0.58	0.83	0.09	0.01			10
Maximum	84.92	44.32	53.38	20.33	2.59	8.64	1.73	9.89	6.20	0.28			10
2.2. Straws (HAS)													
Mean	43.94	14.13	24.49	4.13	2.71	4.66	1.42	3.01	1.35	0.16	100.00	0.09	9
Minimum	7.87	2.46	12.59	0.98	0.10	1.67	0.41	1.18	0.16	0.02		0.02	9
Maximum	77.20	30.68	38.14	10.38	5.57	14.10	2.82	4.93	3.52	0.33		0.28	9
2.3. Other residues (HAR)													
Mean	24.47	16.58	28.25	7.27	4.90	6.62	4.84	3.80	3.05	0.22	100.00	0.16	25
Minimum	2.01	0.97	2.29	0.54	0.11	0.19	0.22	0.01	0.12	0.01		0.02	25
Maximum	94.48	44.13	63.90	31.06	14.60	16.21	36.27	14.74	26.20	2.02		0.46	25
3. Animal biomass (AB)													
Mean	2.90	49.04	7.67	28.17	1.69	2.75	0.35	3.91	3.50	0.02	100.00	0.05	2
Minimum	0.02	41.22	3.16	15.40	1.01	1.38	0.25	3.59	0.60	0.01		0.01	2
Maximum	5.77	56.85	12.19	40.94	2.37	4.11	0.45	4.24	6.41	0.03		0.09	2
4. Mixture of biomass (MB)													
Mean	44.19	17.48	6.00	5.72	10.82	3.52	6.34	2.66	2.53	0.74	100.00	0.16	4
Minimum	34.75	11.51	3.11	1.08	9.77	2.31	4.19	1.88	1.25	0.52			4
Maximum	57.83	25.70	7.76	18.07	11.35	4.77	10.44	4.62	3.18	0.95			4
5. Contaminated biomass (CB)													
Mean	35.73	18.30	3.45	3.64	15.41	3.60	9.78	3.45	1.90	4.74	100.00	0.15	8
Minimum	3.39	7.63	0.16	0.20	3.08	1.57	0.82	0.99	0.54	0.32		0.02	8
Maximum	60.10	26.81	9.70	15.88	53.53	6.45	22.18	10.55	4.06	27.58		0.23	8
All varieties of biomass (AVB)													
Mean	29.76	25.27	17.91	5.71	5.51	5.42	4.00	3.28	2.48	0.66	100.00	0.75	86
Minimum	0.02	0.97	0.16	0.20	0.10	0.19	0.22	0.01	0.09	0.01		0.01	86
Maximum	94.48	83.46	63.90	40.94	53.53	16.21	36.27	14.74	29.82	27.58		3.57	86
Natural biomass (NB)													
Mean	29.14	25.99	19.40	5.92	4.49	5.60	3.41	3.27	2.54	0.24	100.00	0.81	78
Minimum	0.02	0.97	2.19	0.54	0.10	0.19	0.22	0.01	0.09	0.01		0.01	78
Maximum	94.48	83.46	63.90	40.94	15.12	16.21	36.27	14.74	29.82	2.02		3.57	78
Aquatic biomass (A)													
Marine macroalgae	1.65	12.39	15.35	9.76	0.85	12.50	1.87	25.74	19.88	0.01	100.00	0.03	11
Solid fossil fuels													
Peat	37.53	9.97	1.12	2.75	20.14	2.14	13.83	12.11	0.10	0.31	100.00	0.08	1
Lignite (mean)	44.87	13.11	1.48	0.20	17.11	2.50	10.80	8.64	0.48	0.81	100.00	0.07	5
Sub-bituminous coal (mean)	54.74	7.05	1.67	0.08	22.86	2.14	5.30	4.07	1.09	1.00	100.00	0.05	10
Bituminous coal (mean)	56.14	4.90	1.61	0.22	24.82	1.55	6.68	2.16	0.77	1.15	100.00	0.05	22
Coal (mean)	54.06	6.57	1.60	0.50	23.18	1.83	6.85	3.54	0.82	1.05	100.00	0.05	37
Coal (minimum)	32.04	0.43	0.29	0.10	11.32	0.31	0.79	0.27	0.09	0.62		0.02	37
Coal (maximum)	68.35	27.78	4.15	1.70	35.23	3.98	16.44	14.42	2.90	1.61		0.18	37

matter on ash basis, respectively. Then, all peak heights for the characteristic diffraction patterns of each crystalline phase were also measured and the ratios for minerals in a sample were normalized to crystalline matter content and reported as weight % of each mineral on ash basis. It should be noted that IAM is represented in BAs mainly by glass at higher temperatures and non-glass amorphous material at lower temperatures [5]. Finally, the approach and combination of methods used in the present study is the same that has been applied previously for the evaluation of phase–mineral transformations during coal combustion at different temperature ranges [6]. As a result of that, it was possible to use the data for some comparisons between coal ashes and biomass ashes in the present work.

3. Results and discussion

3.1. Chemical classification of inorganic matter in biomass and biomass ash

The reference investigations show that the inorganic composition of biomass and BA is highly variable ([1–5] and references therein). It was demonstrated in the previous overviews [1–5] that the assignment of various biomass varieties to different: (1) groups and sub-groups by origin; and (2) types and sub-types by organic and inorganic composition; could have primary importance for use of biomass fuels and their conversion products. Therefore, a new chemical classification of the inorganic matter of biomass

Table 2
Data for eight biomass samples (air-dried basis), wt.% (indicated otherwise).

Characteristic	Rice husks	Switchgrass	Corn cobs	Plum pits (weathered)	Marine macroalgae	Beech wood chips	Walnut shells	Sunflower shells
Code	RH	SG	CC	PP	MM	BC	WS	SS
Organic type	CHL	CHL	CHL	LCH	HCL	CHL	LCH	CHL
Inorganic type	S	S	K	CK	K	C	CK	K
Inorganic sub-type	S-HA	S-MA	K-LA	CK-LA	K-LA	C-LA	CK-LA	K-LA
Source	Kovachevo, Bulgaria	Mead, Nebraska, USA	Debnevo, Bulgaria	Debnevo, Bulgaria	Tsarevo, Bulgaria	JRS Rosenberg, Germany	Debnevo, Bulgaria	Billa Sofia, Bulgaria
Collection time	08.2007	2003	08.2008	08.2008	08.2009	01.2009	08.2008	08.2008
Note	Cleaned from sand and soil grains	Two mixed harvests (50:50 vol%)		Weathered for 1 year	Cleaned from sand and shell grains	Produced size is 1–4 mm		
Size reduction (mm)	<0.5	<0.5	<1	<1	<0.5	<0.5	<1	<0.5
VM (db)	62.4	80.4	81.1	81.4	47.4	81.6	60.5	76.1
FC (db)	19.1	14.5	16.8	17.9	24.4	17.1	38.6	20.9
A (db)	18.5	5.1	2.1	0.7	28.2	1.3	0.9	3.0
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bulk density (loose) (kg m^{-3})	451	263	412	889	954	454	833	250
Bulk density (shaken) (kg m^{-3})	476	286	435	1000	1250	479	883	275
pH of leachate (solid–liquid = 1:10 mass ratio)	6.66	5.20	5.32	5.57	6.75	5.15	5.28	5.12
Electrical conductivity of leachate (mS/cm)	2.12	1.63	1.60	0.67	19.81	0.70	0.88	3.47
DWR	1.5	7.8	0.8	0.3	15.1	1.4	0.9	2.9
Ash (500 °C/2 h)	18.50	5.14	2.14	0.66	28.24	1.31	0.90	2.97
Ash (700 °C/1 h)	17.48	4.23	1.70	0.52	23.58	0.94	0.77	2.36
Ash (900 °C/1 h)	17.41	4.17	1.47	0.51	20.50	0.86	0.57	1.95
Ash (1100 °C/1 h)	17.37	4.14	1.44	0.50	17.17	0.84	0.52	1.86
Ash (1300 °C/1 h)	17.37			0.47	11.69	0.80	0.51	1.67
Ash (1500 °C/1 h)	17.22							
Fluid AFT observed (°C)	>1500	⩽1100	⩽1100	⩽1300	⩽1300	⩽1300	⩽1300	⩽1300
Fluid AFT by DTA (°C)	>1500	1193	1235	1233	1240	1300	1230	1236
Ash (500 °C/2 h) bulk density (loose) (kg m^{-3})	270	80	200	130	430	170	150	120
HTA (500 °C/2 h)								
SiO_2	89.86	62.90	36.67	12.01	5.60	5.48	2.84	1.45
CaO	1.40	7.69	2.12	43.95	22.06	62.58	38.11	15.57
K_2O	4.16	18.77	47.57	16.29	7.56	18.00	49.33	49.84
P_2O_5	0.60	2.44	4.82	10.17	0.97	2.49	2.37	6.54
Al_2O_3	1.04	0.89	0.81	2.57	0.98	0.49	0.52	0.12
MgO	0.49	4.20	1.97	4.18	7.69	7.49	3.80	11.87
Fe_2O_3	0.41	0.42	1.50	1.75	0.69	0.36	0.40	1.32
SO_3	1.31	2.17	3.44	7.72	28.49	0.77	2.03	11.39
Na_2O	0.23	0.11	0.28	0.79	14.07	0.11	0.12	0.22
TiO_2	0.02	0.04	0.06	0.16	0.03	0.03	0.05	0.01
Cl_2O	0.21	0.23	0.69	0.27	11.84	0.09	0.38	1.60
MnO	0.27	0.14	0.07	0.14	0.02	2.11	0.05	0.07
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
DAI	10.85	1.81	0.65	0.21	0.27	0.07	0.04	0.03
Reference data ([1,2] *and references therein*)								
VM (db)	62.8	80.4	81.2	80.8	50.5	82.0	59.3	76.0
FC (db)	19.2	14.5	16.8	17.8	25.9	17.2	37.9	20.9
A (db)	18.0	5.1	2.0	1.4	23.6	0.8	2.8	3.1
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
C (daf)	49.3	49.6	47.8	49.9	41.7	47.2	49.8	50.4
O (daf)	43.6	43.4	45.6	42.4	44.3	46.6	42.4	42.9
H (daf)	6.1	6.1	5.9	6.7	6.0	6.1	6.2	5.5
N (daf)	0.8	0.7	0.5	0.9	2.1	0.1	1.4	1.1
S (daf)	0.08	0.11	0.01	0.08	2.51	0.01	0.09	0.03
Cl (daf)	0.12	0.08	0.23	0.01	3.34	0.01	0.15	0.10
Sum	100.00	99.99	100.04	99.99	99.95	100.02	100.04	100.03
Cel (daf)	43.8	48.7	48.1	23.7	28.5	45.2	28.1	56.5
Hem (daf)	31.6	38.4	37.2	22.0	65.5	32.7	26.6	28.0
Lig (daf)	24.6	12.9	14.7	54.3	6.0	22.1	45.3	15.5
Sum	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Ext (daf)	6.6	8.0	7.0	5.4	15.1	1.1	2.7	2.6

Abbreviations: A, ash yield; AFT, ash-fusion temperature; Cel, cellulose; daf, dry ash-free basis; DAI, detrital/authigenic index (Si + Al + Fe + Na + Ti oxides/Ca + Mg + Mn + K + P + S + Cl oxides); db, dry basis; DTA, differential-thermal analysis; DWR, dry water-soluble residue; Ext, extractives; FC, fixed carbon; Hem, hemicellulose; HTA, high-temperature ash; Lig, lignin; VM, volatile matter.

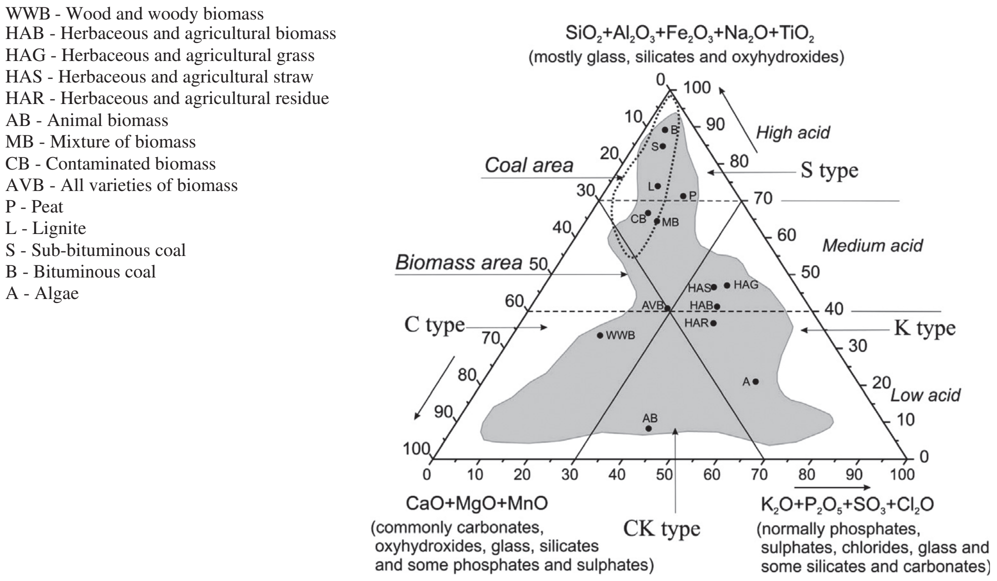

Fig. 2. Areas of 86 biomass varieties plus algae and 38 solid fossil fuels in the chemical classification system of biomass ash, wt.%.

and BA has been generated and reported recently [1]. Shortly, the most abundant six oxides in BAs are those of Si, Al, Ca, Mg, K and P (Table 1) and they were grouped into three couples (Si–Al, Ca–Mg and K–P oxides) according to the positive and negative correlation values among them. The specification of these couples is based on the strong positive correlations between the oxides in the couples and their negative correlations with other oxides. Respectively, the remaining subordinate six oxides or elements are redistributed to the above couples on basis of their strong positive correlations with the oxides in the couples specified. It was found that K has also significant positive correlation with Mg; however, the latter element has stronger positive correlation with Ca (as different Ca–Mg oxalates, carbonates, oxyhydroxides and silicates) than with K (as a limited number of K–Mg minerals or phases) [2,3]. Similar twofold behaviour could also be expected for Na depending on its dominant mobile (salts) or immobile (silicates) occurrence in the system. For example, highly mobile Na can occur in algae, which contain high abundance of this element [1], as well as in some other biomass affected by sea transportation or collected near to sea coasts [2]. In contrast, immobile Na can occur in biomass affected by soil contamination enriched feldspars [2,3]. The specified three oxide associations in the classification (Si + Al + Fe + Na + Ti, Ca + Mg + Mn and K + P + S + Cl); and the defined borders based on their distinctive and highly informative plot distributions (all varieties of biomass, biomass groups and sub-groups and solid fossil fuels with different rank); were applied for the inorganic matter specification in biomass and BA [1–3]. This approach resulted in four chemical biomass ash types (“S”, “C”, “K” and “CK”) further specified into six sub-types (“S-HA”, “S-MA”, “C-MA”, “C-LA”, “K-MA” and “K-LA”) with high, medium and low acid tendencies (Figs. 1d and 2). It should be noted that “CK” type is identical to “CK-LA” sub-type. It was found subsequently that such major associations are also related to the occurrence, content and origin of elements, minerals and phases identified in:

(1) Biomass system, namely: (1) Si–Al–Fe–Na–Ti (mostly as detrital silicates and oxyhydroxides and authigenic opal); (2) Ca–Mg–Mn (commonly as authigenic oxalates and carbonates); and (3) N–K–S–P–Cl (normally as authigenic phosphates, sulphates, chlorides and nitrates) [2].

(2) BA system, namely: (1) Si–Al–Fe–Na–Ti (mostly newly formed glass, silicates and oxyhydroxides); (2) Ca–Mg–Mn (commonly newly formed carbonates, oxyhydroxides, glass, silicates and some phosphates and sulphates); and (3) K–P–S–Cl (normally newly formed phosphates, sulphates, chlorides, glass and some silicates and carbonates) [3].

It was also found that there is a big advantage when the biomass and BA classification systems are based on the identification and implementation of significant relationships between elemental concentrations, combined chemical and phase–mineral associations and especially on an application of genetic approaches for specification of the phases. In this case the reasons for different problems or benefits during biomass processing can be systematically recognized and explained [5]. The above approach, involving composition-based criteria and genetic explanation of the three end members in Fig. 2 is comparable to that used previously for the chemical classification of coal fly ashes [7] and coal HTAs [8], despite the different constituents included as end members and borders used. It was demonstrated that such systematic relationships have a key importance in both fundamental and applied aspects related to potential innovative and sustainable processing of biomass and BA [1–5]. Some of these very interesting and important topics will be discussed in more detail herein.

3.2. Ash fusion behaviour of biomass

3.2.1. General considerations and observations

The reference investigations show that the ash fusion behaviour of different biomass varieties has been studied extensively [9–66]. Unfortunately, the long term experience and knowledge achieved for the ash melting behaviour and phase transformations of coal ash ([6,67,68] and references therein) have not been implemented very successfully in the field of BA. For example, non-existing specific MPs of BAs have been discussed frequently in the literature [9,13,15,17,19–21,26–29,31,35,37–42,44,46,47,50,59,61,66]). It should be stated that MPs occur only for pure (monocomponent) or simple systems, while BA (similar to coal ash) as a multicomponent system of powder material cannot have a specific MP (see for instance [67]). Therefore, BA has three or four characteristic and measurable ash fusion temperatures (AFTs), namely initial

Table 3
Ash-fusion temperatures[a] of biomass groups and sub-groups (90 varieties of biomass) and coals with different rank, °C (based on [3] plus additional data for algae by [46]).

Group, sub-group	DT	ST	HT	FT	Type[b]	Samples[c]
1. Wood and woody biomass (WWB)						
Mean	1192	1328	1380	1407	M	50
Minimum	670	1105	1190	1207	L	50
Maximum	1565	1571	1665	>1700	VH	50
1.1. Stems (WWS)						
Mean	1227	1297	1334	1366	M	20
Minimum	1050	1150	1190	>1190	L	20
Maximum	1453	1525	1665	>1700	VH	20
1.2. Barks (WWBA)						
Mean	1330	1473	~1473	1483	H	13
Minimum	1100	1260	1250	1275	M	13
Maximum	1565	1571	~1574	1576	H	13
1.3. Stumps (WWST)						
Mean	806	1228	1343	1368	M	5
Minimum	670	1105	1191	1207	L	5
Maximum	1191	1360	1460	1490	H	5
1.4. Leaves (WWL)						
Mean	1164	1286	1352	1384	M	4
Minimum	1081	1245	1294	1295	M	4
Maximum	1268	1327	1429	1471	H	4
1.5. Twigs (WWT)						
Mean	1169	1328	1422	1465	H	2
Minimum	1157	1320	1409	1456	H	2
Maximum	1180	1335	1434	1474	H	2
1.6. Roots (WWR)						
Mean	1114	1238	1348	1395	M	2
Minimum	1073	1196	1305	1354	M	2
Maximum	1155	1280	1390	1435	M	2
1.7. Others (WWO)						
Mean	1136	1205	1387	⩾1399	M	4
Minimum	770		1230	1250	M	4
Maximum	1320		1550	>1550	H	4
2. Herbaceous and agricultural biomass (HAB)						
Mean	979	1112	1241	1285	M	34
Minimum	700	795	975	1000	VL	34
Maximum	1472	1513	1605	⩾1620	VH	34
2.1. Grasses and flowers (HAG)						
Mean	970	1127	1308	⩾1314	M	9
Minimum	700	980	1090	1000	L	9
Maximum	1453	1513	1550	⩾1586	H	9
2.2. Straws (HAS)						
Mean	857	1061	1105	1214	L	7
Minimum	700	941	975	1025	VL	7
Maximum	991	1180	1266	1369	M	7
2.3. Stalks (HAST)						
Mean	1049	1181	1222	⩾1244	M	3
Minimum	973	1159	1155	>1155	L	3
Maximum	1154	1202	1288	1335	M	3
2.4. Shells (HASH)						
Mean	798	~798	1310	>1313	M	2
Minimum	775		1225	>1225	M	2
Maximum	820		1395	>1400	M	2
2.5. Husks (HAH) (rice husks)	1472		1605	⩾1620	VH	1
2.6. Pits (HAPT) (olive pits)	1132	1265	1303	1328	M	1
2.7. Other residues (HAR)						
Mean	1023	1150	1238	⩾1278	M	11
Minimum	740	1020	1020	>1020	L	11
Maximum	1260	1280	1380	1500	M	11
3. Contaminated biomass (CB)						
Mean	1174		1280	⩾1283	M	3
Minimum	890		1130	>1130	L	3
Maximum	1438		1505	1510	H	3
4. Aquatic biomass (A) (marine algae)						
Mean	924	1008	1216	1296	M	3
Minimum	747	822	1041	1227	L	3
Maximum	1135	1175	1415	1434	H	3

Table 3 (*continued*)

Group, sub-group	DT	ST	HT	FT	Type[b]	Samples[c]
All varieties of biomass (AVB)						
Mean	1105	1262	1318	1351	M	90
Minimum	670	795	975	1000	VL	90
Maximum	1565	1571	1665	>1700	VH	90
Natural biomass (NB)						
Mean	1103	1262	1319	1354	M	87
Minimum	670	795	975	1000	VL	87
Maximum	1565	1571	1665	>1700	VH	87
Coal						
Lignite (mean)	1147		1261	1286	M	5
Subbituminous coal (mean)	1218		1365	1389	M	10
Bituminous coal (mean)	1280		1404	1423	H	22
Coal (mean)	1251		1388	1411	M	37
Coal (minimum)	1105		1200	1205	L, M	37
Coal (maximum)	1525		1575	1585	H	37

[a] DT, initial deformation temperature; ST, spherical temperature; HT, hemispherical temperature; FT, fluid temperature.

[b] Melting types based on HT: VL, very low (<1000 °C); L, low (1000–1200 °C); M, medium (1200–1400 °C); H, high (1400–1600 °C); VH, very high (>1600 °C) types.

[c] Some of these data are mean values from numerous determinations for a given biomass variety.

deformation (DT), spherical (ST), hemispherical (HT) and flow or fluid (FT) temperatures, because ash melting occurs over a wide temperature range.

Further, the less definitive softening AFT instead of DT or ST is also used in the literature and some standards. This softening AFT seems to be inappropriate because the rounded apex and spherical shape produced from ash cones, pyramids, cubes or cylinders during ash fusion test are not only a result of ash softening, but also due to melting and other phase transformations ([67] and see below). Additionally, the term shrinking AFT (at which the area of the ash test piece falls below 95% of the initial area) is also reported in the literature and prescribed in some standards. However, this term is also inappropriate or less informative because some BAs (especially these enriched in silicates) can show both shrinking and swelling (expansion) over different temperature ranges ([3] and references therein). There are also some problems occurring throughout the AFT test. For example, the advantages or disadvantages of using ash cones, pyramids, cubes or cylinders during an AFT test remain relatively uncertain. Furthermore, the test is performed on preliminary produced ash and normally in air with a heating rate of 5, 7, 8 or 10 °C min^{-1}. It was found that AFTs measured are higher when ash samples for the test are produced at 815 °C than 600 °C (in [60,62] without any explanation). Obviously, the reason for that can be the greater release of some highly volatile elements (Cl, N, S, K, Na, others) from biomass during ash preparation at higher temperatures because portions of such volatile elements do not take part subsequently during the AFT test. It is well known that these volatile elements form typical fluxing components in BA and the using of lower ashing temperature such as 500 °C seems to be more reasonable for sample preparation [5]. On the other hand, the application of reducing atmosphere during AFT test tends to have relatively less significance for natural biomass (in contrast to coal and some contaminated biomass) because it is mostly poor in Fe [1]. Finally, it has been demonstrated that the routine AFT test is an insufficient, and to some extent even subjective method, to characterize reliably and completely the ash fusion properties of a given solid fuel and additional or new approaches and methods are required for that purpose [67]. Despite the above limitations, the ash fusion test currently remains the most commonly used method among others for the evaluation of melting behaviour of any solid fuel.

Table 4
Decreasing orders of mean values for the ash-fusion temperatures (AFTs) of the biomass groups and four solid fossil fuel types (bold font), as well as biomass sub-groups (normal font), °C, Data are for 90 varieties of biomass (based on [3] plus additional data for algae by [46]).

AFT	Order for groups and sub-groups
DT	HAH(1472) > WWBA(1330) > **B**(1280) > **C**(1251) > WWS(1227) > **S**(1218) > **WWB**(1192) > **CB**(1174) > WWT(1169) > WWL(1164) > **L**(1147) > WWO(1136) > HAPT(1132) > WWR(1114) > **AVB**(1105) > **NB**(1103) > HAST(1049) > HAR(1023) > **HAB**(979) > HAG(970) > A(924) > HAS(857) > WWST(806) > HASH(798)
ST	WWBA(1473) > **WWB =** WWT(1328) > WWS(1297) > WWL(1286) > HAPT(1265) > **AVB = NB**(1262) > WWR(1238) > WWST(1228) > WWO(1205) > HAST(1181) > HAR(1150) > HAG(1127) > **HAB**(1112) > HAS(1061) > A(1008) > HASH(795)
HT	HAH(1605) > WWBA(1473) > WWT(1422) > **B**(1404) > **C**(1388) > WWO(1387) > **WWB**(1380) > **S**(1365) > WWL(1352) > WWR(1348) > WWST(1343) > WWS(1334) > **NB**(1319) > **AVB**(1318) > HASH(1310) > HAG(1308) > HAPT(1303) > **CB**(1280) > **L**(1261) > **HAB**(1241) > HAR(1238) > HAST(1222) > A(1216) > HAS(1105)
FT	HAH(1620) > WWBA(1483) > WWT(1465) > **B**(1423) > **C**(1411) > **WWB**(1407) > WWO(1399) > WWR(1395) > **S**(1389) > WWL(1384) > WWST(1368) > WWS(1366) > **NB**(1354) > **AVB**(1351) > HAPT(1328) > HAG(1314) > HASH(1313) > A(1296) > **L**(1286) > **HAB**(1285) > **CB**(1283) > HAR(1278) > HAST(1244) > HAS(1214)

Abbreviations: A, aquatic biomass (marine macroalgae); **AVB**, all varieties of biomass; **B**, bituminous coal; **C**, coal; **CB**, contaminated biomass; DT, initial deformation temperature; FT, fluid temperature; **HAB**, herbaceous and agricultural biomass; HAF, herbaceous and agricultural fibres; HAG, herbaceous and agricultural grasses and flowers; HAH, herbaceous and agricultural husks; HAPT, herbaceous and agricultural pits; HAR, other herbaceous and agricultural residues; HAS, herbaceous and agricultural straws; HASH, herbaceous and agricultural shells; HAST, herbaceous and agricultural stalks; HT, hemispherical temperature; **L**, lignite; **NB**, natural biomass; **S**, sub-bituminous coal; ST, spherical temperature; **WWB**, wood and woody biomass; WWBA, wood and woody barks; WWL, wood and woody leaves; WWO, other wood and woody biomass; WWR, wood and woody roots; WWS, wood and woody stems; WWST, wood and woody stumps; WWT, wood and woody twigs.

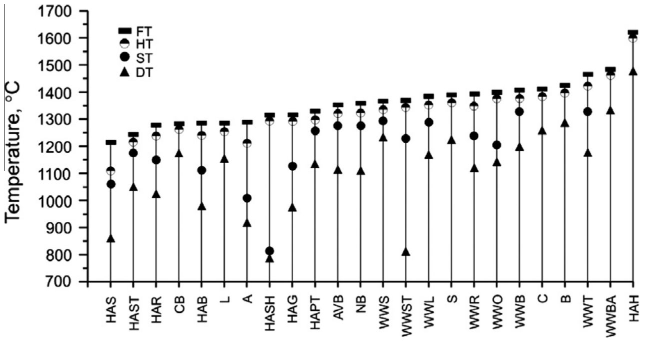

Fig. 3. Mean ash fusion temperatures for the biomass groups and sub-groups and coals based on 90 varieties of biomass and three solid fossil fuel types in increasing order of the fluid temperatures, °C. Abbreviations: A, aquatic biomass; AVB, all varieties of biomass; B, bituminous coal; C, coal; CB, contaminated biomass; DT, initial deformation temperature; FT, fluid temperature; HAB, herbaceous and agricultural biomass; HAF, herbaceous and agricultural fibres; HAG, herbaceous and agricultural grasses and flowers; HAH, herbaceous and agricultural husks; HAPT, herbaceous and agricultural pits; HAR, other herbaceous and agricultural residues; HAS, herbaceous and agricultural straws; HASH, herbaceous and agricultural shells; HAST, herbaceous and agricultural stalks; HT, hemispherical temperature; L, lignite; NB, natural biomass; S, sub-bituminous coal; ST, spherical temperature; WWB, wood and woody biomass; WWBA, wood and woody barks; WWL, wood and woody leaves; WWO, other wood and woody biomass; WWR, wood and woody roots; WWS, wood and woody stems; WWST, wood and woody stumps; WWT, wood and woody twigs.

Table 5

Significant positive (+) and negative (−) correlation coefficient values (R^2) at 95% confidence levels (bold font)[a] and insignificant (normal font) R^2 values for initial deformation (DT), hemispherical (HT) and fluid (FT) ash fusion temperatures and chemical composition of 54 biomass ashes.

Characteristic	Correlation coefficient value with:
DT	(+) **HT(0.74) FT(0.70) CaO(0.50)** TiO$_2$(0.22) Al$_2$O$_3$(0.19) Fe$_2$O$_3$(0.06) (−) **K$_2$O(0.55)** SO$_3$(0.21) P$_2$O$_5$(0.19) SiO$_2$(0.14) Na$_2$O(0.08) MgO(0.01)
HT	(+) **FT(0.98) DT(0.74) CaO(0.55)** Al$_2$O$_3$(0.06) TiO$_2$(0.06) (−) **K$_2$O(0.34) P$_2$O$_5$(0.26)** SiO$_2$(0.23) SO$_3$(0.23) Fe$_2$O$_3$(0.18) Na$_2$O(0.04) MgO(0.01)
FT	(+) **HT(0.98) DT(0.70) CaO(0.52)** TiO$_2$(0.02) Al$_2$O$_3$(0.01) (−) **K$_2$O(0.31) Fe$_2$O$_3$(0.27)** P$_2$O$_5$(0.23) SiO$_2$(0.22) SO$_3$(0.19) Na$_2$O(0.02) MgO(0.00)

[a] The significant R^2 values at 95% confidence level are ⩾0.26 and ⩽−0.26 for 54 variables.

3.2.2. Ash fusion temperatures of biomass and comparisons with coal

The chemical ash composition of 86 varieties of terrestrial biomass and 11 samples of aquatic biomass (marine macroalgae) [1,3], as well as AFTs of 87 varieties of biomass [3] have been reported recently. Therefore, a compilation between both available chemical ash composition and AFTs is used in the present study including also some additional AFT data for: algae [46]; sewage sludge and refuse-derived fuel [51]; sawdust, sorghum chips, spruce and sunflower cake [55]; corn straw, bermuda grass and bamboo [62]; cynara grass [63]; and straw and corn stover [65]. These data are summarized and applied herein for some comparative investigations and establishment of some preliminary major trends and relationships between AFTs and chemical composition of BAs (Tables 1 and 3).

The comparative reference data related to AFTs of biomass and coal have been characterized recently [3]. Shortly, they show that BAs have more variable AFTs in comparison with coal ashes (Table 3). It was also found that there are significant, positive and very strong correlation coefficient (R^2) values among AFTs of 77 varieties of biomass, namely for: (1) DT with ST (0.78) > HT (0.53) > FT (0.50); (2) ST with HT (0.84) > FT (0.82); and (3) HT with FT (0.97) [3]. Hence, there is an almost perfect fit for both HT and FT, while ST and especially DT show more individual behaviour probably due to some different processes responsible for the specific AFTs. It should be noted that such very similar correlations were also identified for coal AFTs [69,70]. These data indicate that the major processes responsible for the characteristic AFTs seem to be similar for both biomass and coal ashes. Some general observations related to the very important AFTs (DT, HT and FT) of biomass and coal are shortly given below based on the data reported earlier ([3] plus additional data for algae [46]).

The DT value of BAs (Table 3) varies over the large range of 670–1565 °C (mean 1105 °C). In contrast, the DT value of coal ashes (Table 3) is in the relatively narrow range of 1105–1525 °C (mean 1251 °C). The mean DT value decreases in the order: bituminous coal > sub-bituminous coal > wood and woody biomass > contaminated biomass > lignite > herbaceous and agricultural biomass > aquatic biomass (Table 4 and Fig. 3). Hence, DT mostly has a much lower value in BA than in coal ash. The low DT is characteristic of some biomass groups and sub-groups such as herbaceous and agricultural shells, straws, grasses, stalks and other residues, as well as wood and woody stumps and aquatic biomass. The extremely low DT is typical of some biomass varieties, namely eupatorium and xanphium stumps, alfalfa, safflower, wheat–barley straw and algae. In contrast, the high DT is characteristic of some biomass sub-groups such as agricultural husks and wood and woody barks and stems. The exceptionally high DT is typical of some biomass varieties, namely balsam bark, hemlock bark, poplar bark, maple (hard) bark, rice husks, willow stems and reed canary grass.

The HT value of BAs (Table 3) varies over the large range of 975–1665 °C (mean 1318 °C). In contrast, the HT value of coal ashes (Table 3) is in the relatively narrow range of 1200–1575 °C (mean 1388 °C). The mean HT value decreases in the order: bituminous coal > wood and woody biomass > sub-bituminous coal > contaminated biomass > lignite > herbaceous and agricultural biomass > aquatic biomass (Table 4 and Fig. 3). Hence, HT normally has a lower value in biomass ash than in coal ash. The low HT is characteristic of some biomass groups and sub-groups such as aquatic biomass, herbaceous and agricultural straws, stalks, pits, grasses, shells and other residues. The extremely low HT is typical of some biomass varieties, namely algae, wheat–barley, barley, oat and rye straws, corn cobs and grass. In contrast, the high HT is characteristic of some biomass sub-groups such as agricultural husks and wood and woody barks and twigs. The exceptionally high HT is typical of some biomass varieties, namely spruce stems, rice husks, balsam bark, maple (hard) bark, tree prunings, alfalfa and reed canary grass.

The FT value of BAs (Table 3) varies over the large range from 1000 to >1700 °C (mean 1351 °C). In contrast, the FT value of coal ashes (Table 3) is in the relatively narrow range of 1205–1585 °C (mean 1411 °C). The mean FT value decreases in the order: bituminous coal > wood and woody biomass > sub-bituminous coal > aquatic biomass > lignite > herbaceous and agricultural biomass > contaminated biomass (Table 4 and Fig. 3). Hence, FT normally has a lower value in biomass ash than in coal ash. The low FT is characteristic of some biomass groups and sub-groups such as aquatic biomass, herbaceous and agricultural straws, stalks, shells, grasses, pits and other residues (similar to HT). The extremely low FT is typical of some biomass varieties, namely corn cobs, stalks and fodder, banagrass, wheat–barley and barley straws, paper pellets, grass and cynara grass. In contrast, the high FT is characteristic of some biomass sub-groups such as agricultural husks and wood and woody barks and twigs (similar to HT). The exceptionally high FT is typical of some biomass varieties, namely spruce and willow stems, balsam bark, beech bark,

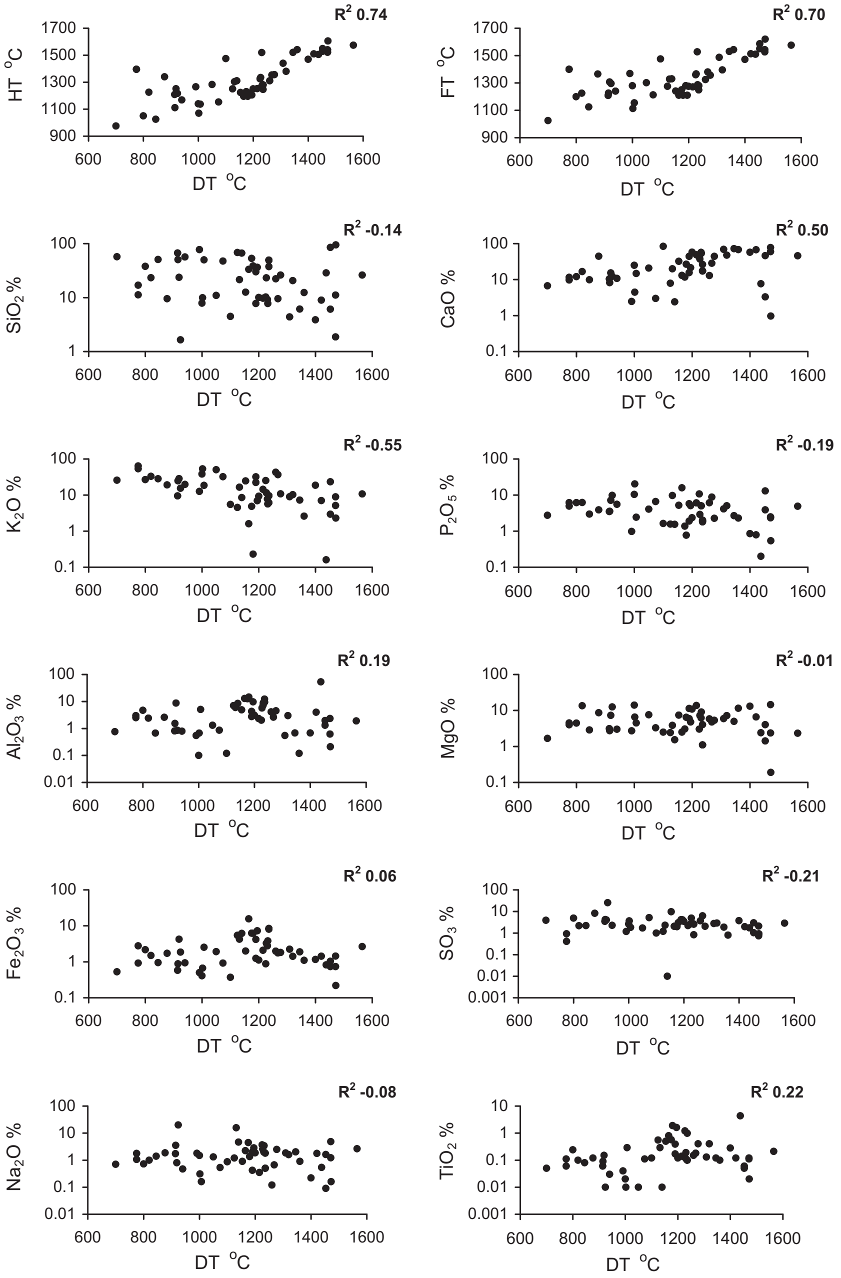

Fig. 4. Correlations between the chemical composition (wt.%) and initial deformation (DT) ash fusion temperature (°C) for 54 varieties of biomass.

hemlock bark, maple (hard) bark, pine bark, poplar bark and spruce bark, as well as tree prunings, rice husks, reed canary grass, alfalfa, sugar cane baggase and paper sludge.

Hence, AFTs of biomass are more variable than of coal and they are normally lower, excluding certain lignites and biomass varieties from "S" and "C" ash types. For comparison, BAs can be divided proximately into three: (1) low (1200 °C); (2) medium (1200–1400 °C); and (3) high (1400–1600 °C) melting types; or ultimately into five: (1) very low (1000 °C); (2) low (1000–1200 °C); (3) medium (1200–1400 °C); (4) high (1400–1600 °C); and (5) very high (>1600 °C) melting types (Table 3); according to HT (the most informative AFT), similar to coal ashes [67].

3.2.3. Relationships between ash fusion temperatures and inorganic composition of biomass and coal

Several steps were undertaken for some initial clarification of relationships between the ash fusion and inorganic composition of biomass. Data compilations between the available: (1) chemical compositions for 61 BAs from totally 87 [1,3]; and (2) AFTs values for 61 BAs from totally about 100 ([3,46,51,55,62,63,65] plus some own studies in Table 2) for the same or similar varieties; were applied as a database herein. As a result of that, data sets for 54, 55, 60 or 61 BAs due to some incomplete DT, HT or FT values were used. However, it should be stated that this compilation of data for many biomass varieties is not from parallel chemical and AFT investigations and in some cases even a subjective approach was applied for a combination of similar biomass varieties. Therefore, these relatively insecure data were used only to establish some preliminary major trends and relationships between AFTs and chemical composition of BAs. For that purpose, all data were arranged just into three very large DT and HT temperature ranges (low, medium and high) below and mostly their average values were considered to diminish the uncertainties to a maximum extent and to simplify the system as much as possible.

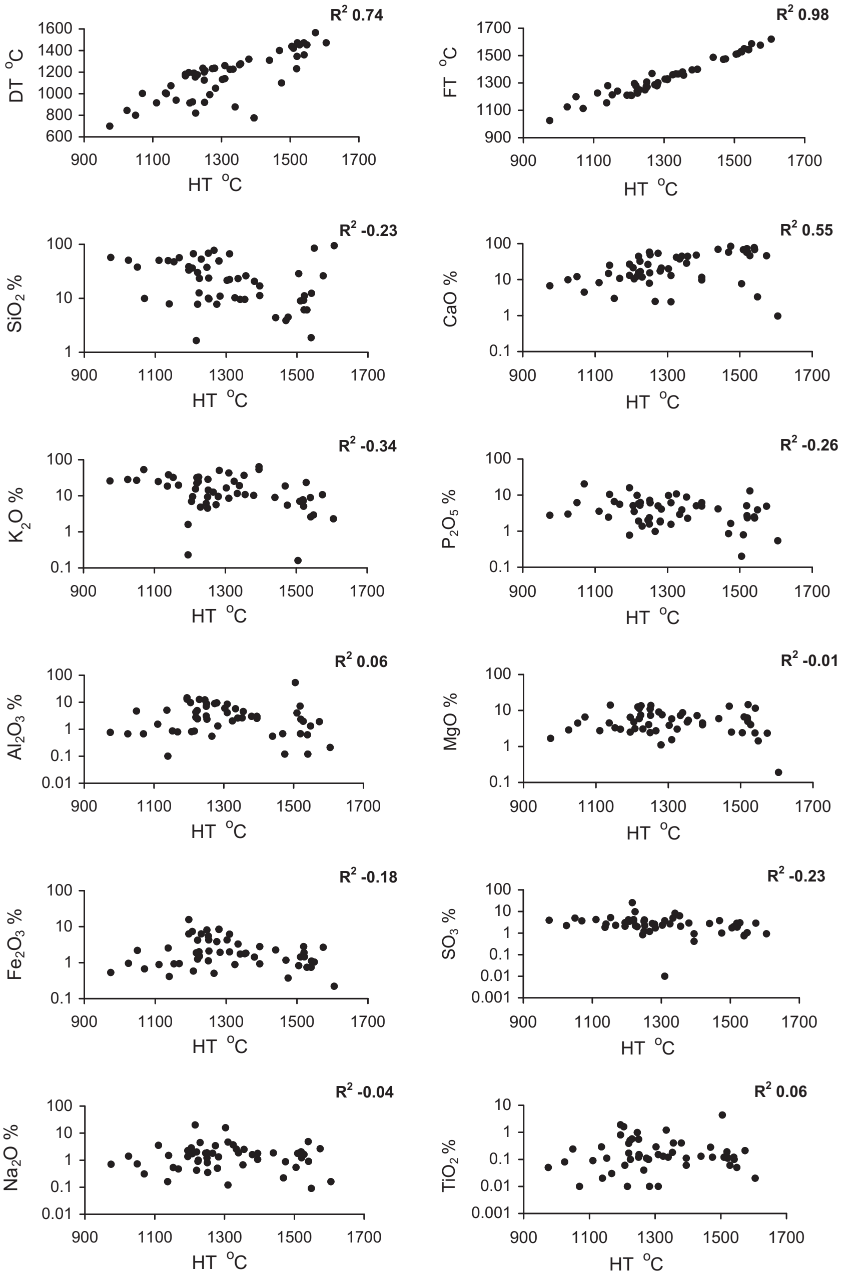

Fig. 5. Correlations between the chemical composition (wt.%) and hemispherical (HT) ash fusion temperature (°C) for 54 varieties of biomass.

As a first step, it was found that there are significant, positive and strong correlation coefficient (R^2) values among the complete DT, HT and FT of 54 BAs (Table 5 and Figs. 4 and 5), namely for: (1) DT with HT (0.74) > FT (0.70); and (2) HT with FT (0.98). Hence, these R^2 values and orders, respectively, are comparable or identical to those mentioned above for 77 biomass varieties. Such correlations indicate the similarity among the major processes responsible for AFTs. There is again an almost perfect fit for both HT and FT and thus the latter AFT will not be discussed separately or in detail below.

As a second step, some positive and negative correlation trends between the most important AFTs, namely DT and HT, and oxide components in the above 54 BAs were also identified herein (Table 5 and Figs. 4 and 5) and they require additional clarification. The correlation analysis shows that: (1) Ca, and to some extent, Al and Ti normally contribute to higher AFTs; whereas (2) K, to a lesser extent, Si, P and S, and occasionally Fe, Na and Mg commonly contribute to lower AFTs in the biomass system (Table 5 and Figs. 4 and 5). Certainly, the above elements represented by their bearing minerals (in which the elements are present) in BA can reveal diverse impact for higher or lower AFTs depending of the mineral species found (see Section 3.2.4). The comparison between AFTs and chemical composition of BA and coal ash shows that there are some important differences related to the contribution of the individual elements and their bearing phases for the specific AFTs in both systems. For example, it is widely accepted that the higher contents of Si, Al and Ti, and lower values of Ca, Fe, Mg, S, Na and K are leading for increased AFTs for coal [67]. On the other hand, the greater concentrations of Ca, Al and Ti and lower contents of K, Si, P, S, Fe, Na and Mg, excluding some highly enriched in Si varieties (rice husks, reed canary grass and others [1]), normally contribute to increased AFTs of biomass. Additionally, sub-trends following the major positive or negative trends between AFTs and ash composition (SiO_2, CaO, K_2O, P_2O_5, Al_2O_3, MgO, Fe_2O_3, Na_2O, TiO_2) can also be seen (Figs. 4 and 5). The reason for such sub-trends is mostly associated with biomass varieties belonging to specified: (1) biomass groups and sub-groups by origin; or (2) inorganic biomass types and sub-types.

As a third step, the most important AFTs, namely DT (for 55 BAs) and HT (for 60 BAs) were arranged into three low, medium and high DT (1100, 1100–1300 and >1300 °C) and HT (1200, 1200–1400 and >1400 °C) groups (Tables 6 and 7) to find or confirm also some general tendencies. These three DT and HT groups were selected due to their importance for possible occurrence of severe, significant or limited slagging problems, respectively, during pulverized biomass co-combustion with coal and other solid fuels (see Section 3.4.1.3 and [4]). For the above purpose, the mean values of these DT and HT groups and their average chemical composition were used to illustrate certain major trends among them (Figs. 6 and 7). Such trends, which are similar to those in Figs. 4 and 5, are applicable for some preliminary and proximate DT and HT prediction purposes related to BAs and involving all oxide components, similar to coal ashes [67].

As a fourth step, the composition and DT and HT values for 55 and 60 BA varieties, respectively, were plotted on the chemical classification system of BAs to find the distribution of the three low, medium and high DT and HT groups (Figs. 8 and 9). As a result, quite informative distributions of the samples in low (mainly "K-MA", "K-LA" and "S-MA", and partly "CK-LA" and "S-HA" sub-types), medium (all types and sub-types) and high (mostly "C-LA" and "S-HA" and partly "CK-LA" sub-types) DT and HT areas on the triangle graph are observed. It can be seen that the low DT and HT of biomass varieties are located to the right positions on the triangle graph for "K-MA", "K-LA", "S-MA", "CK-LA" and "S-HA" sub-types (Figs. 8 and 9). Such distributions are also applicable for some preliminary and proximate DT and HT prediction purposes of BAs (see also Section 3.4.1), similar to coal ashes [67].

Finally, the preliminary major tendencies and relationships found above cannot be exclusive or complete and future use of more secure (complete and parallel) and larger number of samples may provoke some changes in the trends defined herein. Moreover, the approach described above can be used for future evaluation of such chemical and AFT trends and relationships based on more secure data.

3.2.4. Ash fusion mechanisms of biomass and coal

It is well known that the defined DT, HT and FT of coal ashes fit various processes of inorganic transformations [67]. For example, the reference investigations show that DT corresponds to a considerable initial deformation of ashes (shrinkage, expansion, agglomeration, sintering, softening, stickiness) as a result of mineral transformations (anhydrite decomposition, intensive crystallization of mullite, cristobalite, corundum and others) and initial localized softening (quartz) and melting of some minerals (Na–K–Mg–Fe chlorides, sulphides–sulphates and nitrates, plagioclases, K feldspars, clay and mica minerals, Fe oxides, others) in the system. Further, HT is connected with considerable melting of most minerals as a result of the intensive liquid formation and dissolution of the more refractory minerals by the initial melts, as well as some changes in viscosity and flow properties of the plastic phases and melts in the system. Finally, FT is related to the rate of complete melting and dissolution of the most refractory minerals and their products (quartz, cristobalite, metakaolinite, mullite, Ti and Al oxides, spinels, lime, periclase, others), as well as to the intensive flow

Table 6

Ash fusion temperatures (°C) and chemical ash composition (wt.%) for 55 varieties of biomass arranged into three initial deformation (DT) temperature ranges (based on data from [1,3] and additional ash fusion data by [46,51,55,62,63,65]).

DT range	DT	HT	FT	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	Samples
<1100														
Mean	916	1189	1247	33.01	13.04	30.00	7.28	2.32	5.98	1.86	4.28	2.14	0.09	19
Minimum	700	975	1025	1.65	2.46	9.49	0.98	0.10	1.67	0.41	0.41	0.14	0.01	
Maximum	1074	1395	1400	77.20	44.32	63.90	31.06	8.75	14.10	9.23	25.74	19.88	0.29	
1100–1300														
Mean	1200	1287	1306	27.67	31.34	13.78	4.58	6.74	5.40	4.51	3.06	2.46	0.47	23
Minimum	1100	1195	1210	4.48	2.41	0.23	0.77	0.12	1.10	0.37	0.01	0.12	0.01	
Maximum	1277	1519	1527	68.18	83.46	42.79	15.88	14.54	13.80	15.70	9.70	15.77	1.90	
>1300														
Mean	1421	1514	1527	23.81	47.89	8.33	3.32	5.45	5.89	1.30	2.04	1.50	0.47	13
Minimum	1309	1380	1395	1.86	0.97	0.16	0.20	0.12	0.19	0.22	0.74	0.09	0.02	
Maximum	1565	1605	1620	94.48	77.31	23.40	13.01	53.53	14.57	2.65	3.77	4.84	4.37	

Table 7

Ash fusion temperatures (°C) and chemical ash composition (wt.%) for 60 varieties of biomass arranged into three hemispherical (HT) temperature ranges (based on data from [1,3] and additional ash fusion data by [46,51,55,62,63,65]).

HT range	DT	HT	FT	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	Samples
<1200														
Mean	966	1101	1161	41.88	11.45	25.25	6.49	3.52	4.52	2.62	2.90	1.07	0.31	13
Minimum	700	975	1000	7.87	2.98	0.23	0.77	0.10	1.67	0.41	0.83	0.16	0.01	
Maximum	1180	1195	1280	66.25	26.81	53.38	20.33	14.54	14.10	15.70	5.17	3.52	1.90	
1200–1400														
Mean	1113	1284	1306	25.69	26.41	20.58	6.58	4.67	6.09	3.04	3.83	2.83	0.28	32
Minimum	775	1205	1208	0.02	2.41	3.16	0.98	0.11	1.10	0.25	0.01	0.12	0.01	
Maximum	1320	1395	1400	77.20	57.74	63.90	40.94	12.64	13.80	8.49	25.74	19.88	1.60	
>1400														
Mean	1392	1520	1531	23.29	48.02	7.89	3.24	5.99	5.51	1.98	2.07	1.49	0.53	15
Minimum	1100	1440	1472	1.86	0.97	0.16	0.20	0.12	0.19	0.22	0.74	0.09	0.02	
Maximum	1565	1605	1620	94.48	83.46	23.40	13.01	53.53	14.57	11.12	3.77	4.84	4.37	

changes (viscosity, surface tension, rate of flow) of the liquid and plastic phases in the system. It should be noted that ashes with an identical chemical composition can frequently demonstrate different ash melting behaviour as a result of diverse mineral composition. Samples with similar and even identical mineral composition can occasionally exhibit different ash fusion characteristics due to diverse: (1) size and morphology of the minerals; (2) association of the minerals in aggregates, particles and agglomerates; (3) isomorphic substitution and other element impurities in the minerals; as well as (4) sample preparation, heating rate, atmosphere and other factors [67]. Therefore, a reliable explanation and prediction of AFTs in some cases is complicated without considering such factors.

Most of the above coal ash transformations responsible for AFTs are also valid for BAs despite some significant differences. It was found that AFTs of biomass are more variable than coal and they are normally lower (excluding some lignites and biomass varieties from “S” and “C” types) [3]. Certain indicative trends of natural biomass in comparison with coal were identified recently [2], namely the potential of biomass to have normally:

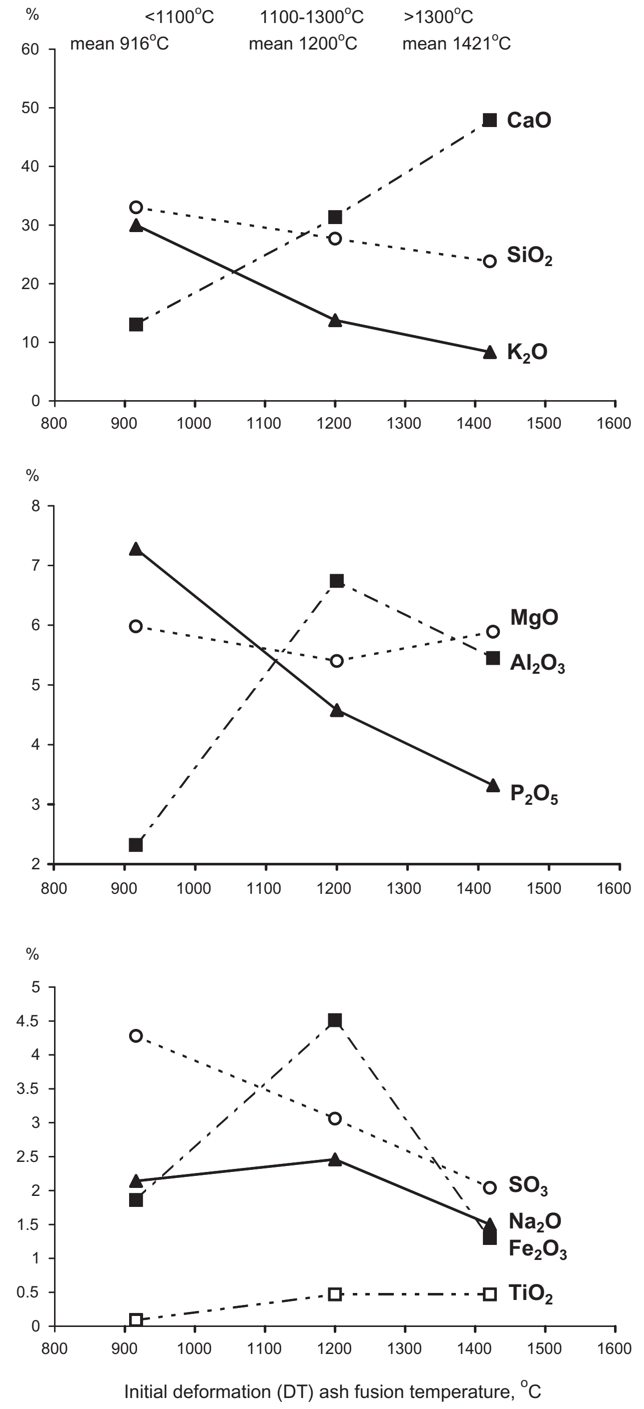

Fig. 6. Mean contents of the chemical components and mean initial deformation (DT) ash fusion temperatures (916, 1200 and 1421 °C) for three temperature ranges (<1100, 1100–1300 and >1300 °C) based on 55 varieties of biomass.

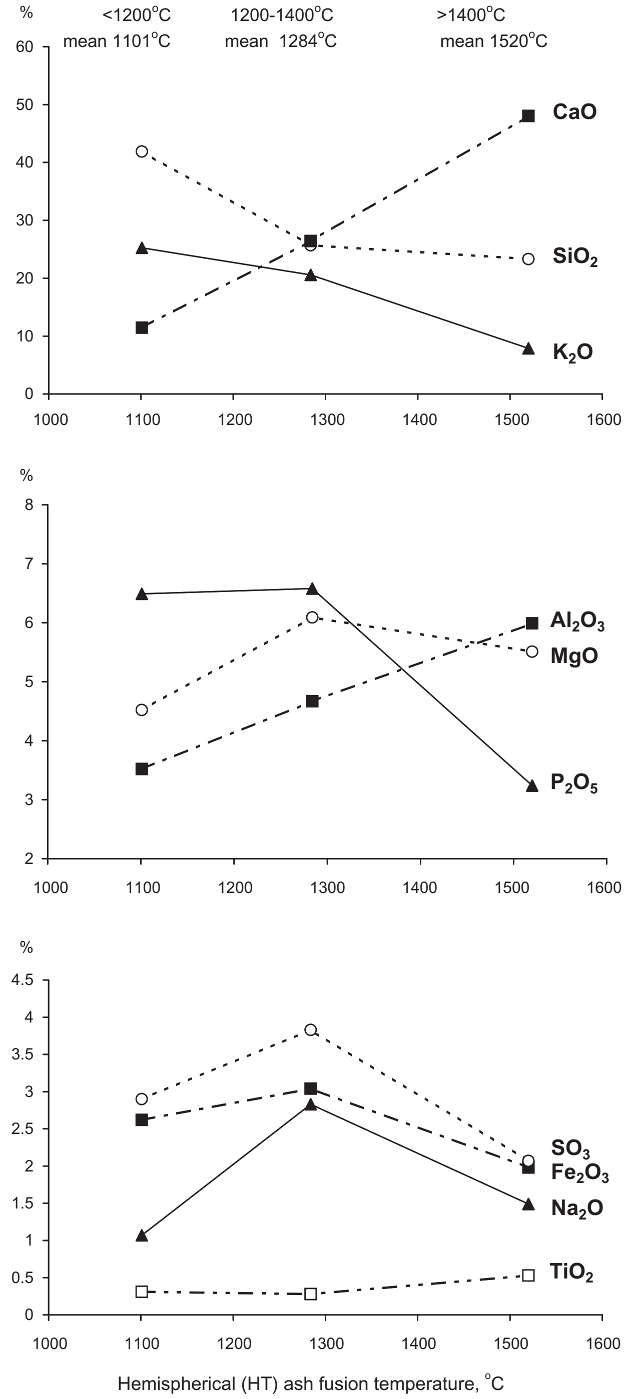

Fig. 7. Mean contents of the chemical components and mean hemispherical (HT) ash fusion temperatures (1101, 1284 and 1520 °C) for three temperature ranges (<1200, 1200–1400 and >1400 °C) based on 60 varieties of biomass.

(1) Higher values of Ca, Cl, H, K, Mg, Mn, Na, O, P, carbonates, chlorides, phosphates, organically bound inorganic elements and water-soluble components.
(2) Lower values of Al, C, Fe, N, S, Si, Ti, inorganic matter, oxyhydroxides, silicates and sulphates–sulphides.

Such differences are reasons for the lower AFTs of biomass in comparison with coal. For instance, it is widely accepted that the higher contents of refractory Si-, Al- and Ti-bearing minerals and lower concentrations of fluxing Ca-, Fe-, Mg-, S-, Na- and K-containing minerals are normally responsible for increased AFTs of coal [67]. On the other hand, the high contents of Ca-, Al- and Ti-bearing minerals and low concentrations of K-, Si-, P-, S-, Fe-, Na- and Mg-containing minerals (excluding the highly enriched in Si biomass varieties) are commonly responsible for increased AFTs of biomass according to chemical trends specified above (see Section 3.2.3 and Figs. 3–7). It should be noted that the minerals and phases in biomass and BA can have dual fluxing (with MPs 1200 °C) or refractory (with MPs >1200 °C) behaviour during thermo-chemical conversion of biomass and this twofold behaviour is also characteristic for the major and minor elements in IM of biomass and BA (Table 8). Therefore, the most significant difference between the ash fusion behaviour of coal and biomass is related to the diverse fluxing and refractory roles of the major elements (especially Si, Al, Ca and K) represented by their bearing minerals in both systems.

The reference investigations show that melt formation in combustion products can initiate at different temperatures depending on the phase composition of biomass and BA. For example, the fusion of: (1) K and Na nitrates and hydroxides (500 °C); (2) some low-temperature K–Na silicate eutectics and Fe and Mn chlorides (500–700 °C); (3) K and Na chlorides and carbonates, as well as Na sulphate (700–900 °C); (4) K sulphate (900–1100 °C); (5) Mg sulphate, acid plagioclases, feldspars, illite and montmorillonite (1100–1300 °C); (6) Ca sulphate and basic plagioclases (1300–1500 °C); and (7) Ca and Mg silicates and oxides, kaolinite and silica minerals (>1500 °C); can be the major reasons for the initial liquid formation with increasing temperatures [5]. Additionally, it was found that the first evidence of melting of BA was determined as much as 150 °C below DT [71].

The present study shows that the low AFTs (especially HT) are characteristic of numerous BAs which belong to “K”, “S” and “CK” types and particularly to “K-MA”, “K-LA”, “S-MA” and partly “CK-LA” sub-types (Table 9 and Figs. 8 and 9). In contrast, other BAs from “S” and “C” types and especially “C-LA”, “S-HA” and partly “CK-LA” sub-types show higher AFTs (Table 9 and Figs. 8 and 9). The influence of mineral and chemical composition of BAs on their fusibility is probably similar to that of coal ashes [6,67,68,72]. For instance, there are two leading mechanisms [67,72] that explain the distinct ash fusion behaviour of coal, namely:

(1) “Melting–dissolution”.
(2) “Softening–melting”.

The first mechanism is related to the formation of initial and active low-temperature melts with low viscosity (high mobility) that quickly dissolve the residual refractory minerals or phases in the system. The second mechanism is connected with prolonged softening and subsequent melting of solid phases and formation of less active and high-temperature melts with high viscosity (low mobility) that result in sluggish flow and depressed dissolution of the residual refractory constituents in the system. It was postulated that the mechanism “melting–dissolution” seems to be more typical for BAs compared to coal ashes that exhibit the more characteristic “softening–melting” mechanism [4]. However, it should be stated that the above major mechanisms are valid for silicate systems like coal ashes and BAs with high acid and partly medium acid tendencies (see coal ash and BA areas in Fig. 2), whereas most BAs belong to more complex oxide–carbonate–phosphate–chloride–sulphate systems plus silicates. Therefore, the initial and final alterations, as well as the slow or high flow variations of BAs are a result of more complex phase–mineral transformations, softening, melting, dissolution and viscosity changes of the solid, plastic and liquid phases in the system.

The present study indicates that the above mechanisms can be applied to BAs, however, additional ash fusion mechanisms and sub-mechanisms related to BAs can also occur. Their existence is due to the much more variable composition and AFTs of biomass in comparison with coal. For example, some significant differences between the temperature ranges of specific AFTs of BAs and coal ashes were observed. It can be seen that the temperature range between DT and FT (related to the initial and final alterations in the system) is normally 139–171 °C for coal ashes and larger for BAs, namely 22–293 °C (Tables 3, 4, 6, 7 and 9). Similar observation is also valid for the temperature range between HT and FT (connected with the final flow changes in the system), which is commonly between 19 and 25 °C for coal ashes and larger for BAs, namely 7–92 °C (Tables 3, 4, 6, 7 and 9). The results show that the mean temperature ranges (°C) between:

(1) DT and FT of BAs decrease in the order “K” (293) > “CK” (160) > “S” (135) > “C” (117) for types and “K-MA” (293) > “K-LA” (289) > “S-HA” (174) > “CK-LA” (160) > “C-LA” (129) > “S-MA” (95) > “C-MA” (22) for sub-types.
(2) HT and FT of BAs decline in the order “K” (49) > “CK” (35) > “S” (18) > “C” (11) for types and “K-MA” (92) > “CK-LA” (35) > “S-HA” (28) > “K-LA” (26) > “C-LA” (11) > “C-MA” (9) > “S-MA” (7) for sub-types.

It can be seen that both orders for BA types and sub-types are identical or similar, respectively. As major trends, BAs with lower AFTs normally show larger temperature ranges between the initial and final transformations and slower flow changes in the system. In contrast, BAs with higher AFTs commonly exhibit shorter temperature ranges between the initial and final transformations in the system and higher flow speed and changes in the system. The common ash fusion mechanisms for BA sub-types (based on the mean values in Table 9) includes:

(1) Medium DT and high HT with moderate softening–melting range and medium flow-dissolution rate for “S-HA”.
(2) Medium DT and HT with short softening–melting range and high flow-dissolution rate for “S-MA”.
(3) Medium DT and HT with short softening–melting range and high flow-dissolution rate for “C-MA”.
(4) High DT and HT with moderate softening–melting range and high flow-dissolution rate for “C-LA”.
(5) Low DT and HT with large softening–melting range and slow flow-dissolution rate for “K-MA”.
(6) Low DT and medium HT with large softening–melting range and medium flow-dissolution rate for “K-LA”.
(7) Medium DT and HT with moderate softening–melting range and medium flow-dissolution rate for “CK-LA”.

Nevertheless, cases such as lower AFTs with active or less active melts, higher AFTs with active or less active melts, as well as low or high softening–melting ranges and slow or high flow-dissolution rates of refractory minerals also occur for specific biomass varieties in the system. The above observations for BAs are somehow not in accordance with the widely accepted statements and explanations for silicate systems such as coal ashes (Table 1 and [67] and references therein). They undoubtedly show that additional ash fusion scenarios also occur in the BA system especially with low and medium acid tendencies. Despite these limitations, the above listed characteristic patterns for biomass types and sub-types are applicable for some preliminary and proximate predictions of ash fusion behaviour related to any solid biomass fuel.

Finally, the composition and AFTs of biomass are much more variable than of coal and the present study also reveals that the simplified generalizations about the ash fusion behaviour of biomass cannot be applied universally for all biomass varieties and their groups and sub-groups by origin, as well as for their chemical types and even sub-types. Therefore, the real ash fusion behaviour of each biomass feedstock has to be evaluated on a case-by-case basis. Despite this, an understanding of some leading trends, similarities or differences, in particular for the various inorganic and AFT types and sub-types, is important and can assist for solving or reducing many technological and environmental problems related to combustion and co-combustion of biomass with coal and other fuels (see Section 3.4). Already, there are ample opportunities for future research in this area.

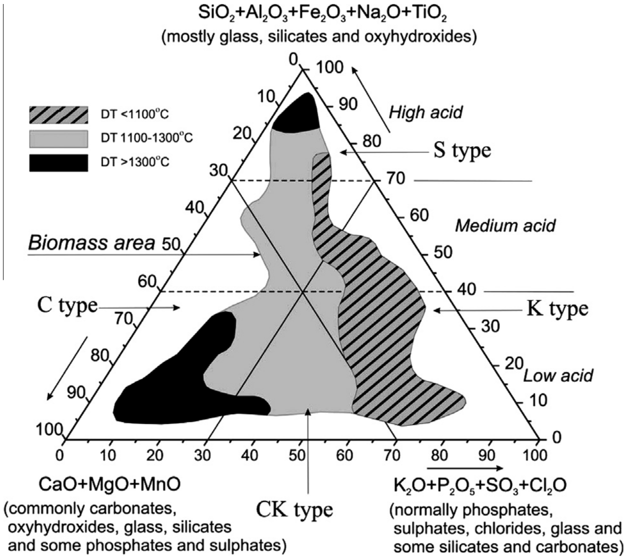

Fig. 8. Areas of low (<1100 °C), medium (1100–1300 °C) and high (>1300 °C) initial deformation (DT) ash fusion temperatures for 55 varieties of biomass in the chemical classification system of biomass ash, wt.%.

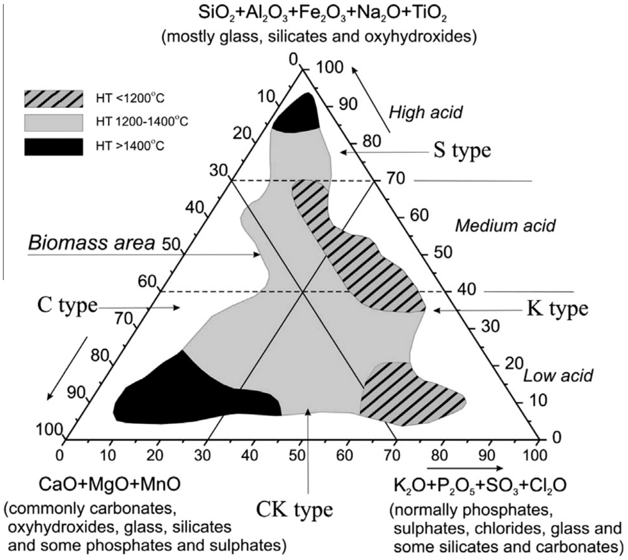

Fig. 9. Areas of low (<1200 °C), medium (1200–1400 °C) and high (>1400 °C) hemispherical (HT) ash fusion temperatures for 60 varieties of biomass in the chemical classification system of biomass ash, wt.%.

3.3. Ash formation mechanisms of biomass types and sub-types

3.3.1. Phase–mineral transformations of organic and inorganic matter and ash formation

The phase–mineral transformations of OM and IM and ash formation during biomass combustion have been characterized in detail in Part I using reference and own data [5]. The formation mechanisms of different mineral classes, glass, amorphous (non-glass) material, char, organic minerals and other inorganic phases in BAs have also been described comprehensively therein [5]. It was generalized in Part I that:

(1) The physico-chemical transformations of OM and IM during biomass combustion include various interactions between solid, gas and liquid phases with original and newly formed origin in such multicomponent systems. General processes, namely: (1) combustion of OM (200–850 °C) (2) fragmentation (disintegration) of particles (500 °C); (3) initial (700–900 °C), significant (700–1100 °C) and extensive (700–1300 °C) agglomeration or occasionally swelling of particles; (4) initial (700 °C), extensive (900–1100 °C) and complete (1100–1500 °C) fusion of particles or minerals with different MPs; (5) various new phase crystallizations (500–1500 °C); and (6) melt/glass formation (700–1500 °C); were observed in BAs.

(2) OM of different biomass varieties tends to show similar combustion behaviour despite different phase and chemical composition, whereas IM of these biomass varieties has a tendency to reveal variable performance during combustion. The investigations also indicate that the thermal behaviour of IM, ash fusion and ash formation mechanisms of different BAs tend to be: (1) diverse between the inorganic “S”, “C”, “K” and “CK” types; and (2) similar within the inorganic types and sub-types specified.

(3) The systematization of physico-chemical transformations during biomass combustion show that the original OM and IM in biomass transform: (1) initially to devolatilization of OM and burning of combustible gases and char with formation of intermediate and less stable oxalates, nitrates, chlorides, hydroxides, carbonates, sulphates and inorganic amorphous (non-glass) material; (2) subsequently to more stable silicates, phosphates and oxides; (3) then to melting accompanied by dissolution of the refractory minerals; with increasing combustion temperatures in the system; and (4) followed by crystallization of melt and formation of glass accompanied by some salt condensation and hydroxylation, hydration and carbonation of newly formed phases during cooling of BA. Finally, some post-combustion transformations of the newly formed minerals and phases to stable species during weathering among silicates, hydroxides, phosphates, sulphates, carbonates, chlorides and nitrates also occur due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air through storage of BA.

(4) The inorganic composition of biomass and BA is highly variable and the assignment of various biomass varieties to different inorganic types and sub-types could have primary importance when predicting the behaviour of a particular

Table 8
Fluxing and refractory behaviour of different modes of element occurrence during combustion of biomass according to the melting point (MP) of minerals and phases containing 11 ash-forming elements, °C (based on [5]).

Element	Fluxing minerals and phases (with MP $\leqslant$ 1200 °C)	Refractory minerals and phases (with MP > 1200 °C)
Si	K–Na silicates (540–1170), K silicates (600–980), K–Mg silicate ($\sim$685), K aluminosilicate ($\sim$695), K–Ca silicates (720–850), Na silicates ($\geqslant$874), zeolites (896–1185), montmorillonite (1000–1300), amphibole (1030–1140), water glass (1088), albite (1118), K feldspars, microcline, orthoclase, sanidine (1170), biotite, chlorite, muscovite ($\sim$1200)	Illite (1200–1300), fayalite (1205), diopside (1392), Ca–Mg silicates (1392–1554), elemental Si (1420), nepheline (1526), Ca silicate hydrate ($\sim$1540–1544[a]), Ca silicates, wollastonite (1540–1544), anorthite (1553), akermanite (1554), enstatite (1557), Mg silicates (1557–1890), gehlenite (1590), kaolinite (1650–1810), kalsilite–kaliophilite (1684–1750), leucite (1686), silica minerals (1713), Cd silicate (1785), andalusite, mullite, sillimanite (1810), forsterite (1890), larnite (2130), zircon (2552)
Ca	Ca–K phosphates (590), K–Ca silicates (720–850), Ca chloride (772), fairchildite–butschliite (815), zeolites (896–1185), montmorillonite (1000–1300), amphibole (1030–1140)	Ca–Fe oxides (1225–1325), chloro–fluoro–apatite (1270), apatite (1270–1660), fluorite (1378), diopside (1392), Ca–Mg silicates (1392–1554), hydroxylapatite (1400[a]), anhydrite, bassanite, gypsum (1450[a]), srebrodolskite (1450), carbonateapatite (1470), Ca–Al oxides (1535), Ca silicate hydrate ($\sim$1540–1544[a]), Ca silicates, wollastonite (1540–1544), anorthite (1553), akermanite (1554), K–Ca phosphate (1560), chloroapatite (1580), gehlenite (1590), fluoroapatite (1660), larnite (2130), lime (2570–2597), portlandite (2570–2597[a])
K	Nitre ($\sim$330), K–Na–Fe chlorides (340–390), K hydroxide (380–406), K–Na sulphate–chloride (515), K–Na silicates (540–1170), Ca–K phosphates (590), K silicates (600–980), K phosphate ($\geqslant$610), K–Mg silicate ($\sim$685), K–Al sulphate (690–800), K aluminosilicate ($\sim$695), K–Ca silicates (720–850), K halite (770–801), sylvite (770–790), K carbonate (788–904), K phosphate ($\sim$800), fairchildite–butschliite (815), K sulphide (835), zeolites (896–1185), arcanite (1067–1100), K–Fe oxide, K–Na–Fe oxide ($\geqslant$1135),K feldspars, microcline, orthoclase, sanidine (1170), biotite, muscovite ($\sim$1200)	Illite (1200–1300), K phosphate (1325–1620), K–Ca phosphate (1560), nepheline (1526), kalsilite–kaliophilite (1684–1750), leucite (1686)
P	Ca–K phosphates (590), K phosphate ($\geqslant$610), K phosphate ($\sim$800)	Chloro–fluoro–apatite (1270), apatite (1270–1660), K phosphate (1325–1620), Mg phosphate ($\sim$1348), hydroxylapatite (1400[a]), carbonateapatite (1470), evansite (>1502), K–Ca phosphate (1560), chloroapatite (1580), fluoroapatite (1660), berlinite (2000)
Al	Elemental Al (660), K–Al sulphate (690–800), K aluminosilicate ($\sim$695), zeolites (896–1185), montmorillonite (1000–1300), amphibole (1030–1140), albite (1118), K feldspars, microcline, orthoclase, sanidine (1170), biotite, chlorite, muscovite ($\sim$1200)	Illite (1200–1300), evansite (>1502), nepheline (1526), Ca–Al oxides (1535), anorthite (1553), gehlenite (1590), kaolinite (1650–1810), kalsilite–kaliophilite (1684–1750), leucite (1686), andalusite, mullite, sillimanite (1810), berlinite (2000), γ-alumina, corundum (2050), gibbsite (2050[a]), spinel (2135)
Mg	K–Mg silicate ($\sim$685), bischofite (714[a]), montmorillonite (1000–1300), amphibole (1030–1140), kieserite dehydrated (1130), biotite, chlorite ($\sim$1200)	Mg phosphate ($\sim$1348), diopside (1392), Ca–Mg silicates (1392–1554), akermanite (1554), enstatite (1557), Mg silicates (1557–1890), forsterite (1890), spinel (2135), brucite (2800[a]), periclase (2800)
Fe	Molysite (300–308), K–Na–Fe chlorides (340–390), rokühnite (677), pyrite (743), chalcopyrite (800–1027), montmorillonite (1000–1300), pyrrhotite (1027–1175), amphibole (1030–1140), K–Fe oxide, K–Na–Fe oxide, Na–Fe oxide ($\geqslant$1135), troilite (1175), biotite, chlorite ($\sim$1200)	Fayalite (1205), Ca–Fe oxides (1225–1325), wustite (1370–1378), srebrodolskite (1450), elemental Fe (1536), goethite (1567[a]), hematite (1567–1594), maghemite (1567–1597), Zn ferrite ($\sim$1590), magnetite (1592–1597), Cr–Fe oxide (1597–1990)
S	Elemental S (112), Cu sulphate (200), orpiment (310), realgar (320), K–Na sulphate–chloride (515), stibnite (546), Na chloride–sulphate ($\geqslant$628), K–Al sulphate (690–800), Mn sulphate (700), molybdenite (730), pyrite (743), chalcopyrite (800–1027), K sulphide (835), thenardite (884), pyrrhotite (1027–1175), arcanite (1067–1100), galena (1097), chalcocite, kieserite dehydrated (1130), anglesite (1170), troilite (1175)	Anhydrite, bassanite, gypsum (1450[a]), barite (1580–2400[a]), Zn sulphide (1775)
Na	Na hydroxide (318), K–Na–Fe chlorides (340–390), nitratine (370), K–Na sulphate–chloride (515), K–Na silicates (540–1170), Na chloride–sulphate ($\geqslant$628), K halite (770–801), halite (801), natrite (850), Na silicates ($\geqslant$874), thenardite (884), zeolites (896–1185), montmorillonite (1000–1300), amphibole (1030–1140), water glass (1088), albite (1118), Na oxide (1132), K–Na–Fe oxide, Na–Fe oxide ($\geqslant$1135), sanidine (1170)	Nepheline (1526)
Ti	Macedonite (1170)	Zn–Ti oxide ($\sim$1549), anatase, brookite, rutile (1827)
Cl	Molysite (300–308), K–Na–Fe chlorides (340–390), K–Na sulphate–chloride (515), Na chloride–sulphate ($\geqslant$628), rokühnite (677), bischofite (714[a]), K halite (770–801), sylvite (770–790), Ca chloride (772), halite (801)	Apatite (1270–1660), chloro–fluoro–apatite (1270), chloroapatite (1580)

[a] After decomposition.

fuel during processing and potential applications of biomass conversion products.

As mentioned above, the specification of IM in biomass resulted in four chemical biomass ash types (“S”, “C”, “K” and “CK”) further specified into six sub-types (“S-HA”, “S-MA”, “C-MA”, “C-LA”, “K-MA” and “K-LA”, as the “CK” type is also identical to “CK-LA” sub-type) with high, medium and low acid tendencies (Fig. 2). The chemical and phase–mineral composition of eight biomass samples (Tables 2 and 10–18) was also studied herein for additional clarification of the ash formation mechanisms of the above listed biomass types and sub-types.

3.3.2. Ash acidity

BAs have high, medium and low acid tendencies based mostly on Si contents expressed as SiO_2 (Fig. 2). It should be stated that this oxide is not a typical component of all BAs (0.02–94% of SiO_2, mean about 30%) in contrast to coal ashes (32–68% of SiO_2,

Table 9
Chemical ash composition (wt.%) for 87 varieties of biomass and ash fusion temperatures (°C) for 61 varieties of biomass arranged in types and sub-types (based on data from [1,3] and additional ash fusion data by [46,51,55,62,63,65]).

Type, sub-type	SiO_2	CaO	K_2O	P_2O_5	Al_2O_3	MgO	Fe_2O_3	SO_3	Na_2O	TiO_2	DT	HT	FT	Samples
1. S type														
Mean	52.87	11.39	6.75	3.52	9.61	2.77	5.75	2.61	3.12	1.59	1191	1308	1326	27
Minimum	3.39	0.97	0.16	0.20	0.21	0.19	0.22	0.01	0.09	0.01	914	1100	1100	
Maximum	94.48	23.92	18.53	18.07	53.53	4.77	22.18	11.66	26.20	27.58	1472	1605	1620	
1.1. S-HA sub-type														
Mean	60.05	7.31	5.40	1.74	11.07	2.40	5.32	2.09	1.98	2.64	1256	1402	1430	14
Minimum	3.39	0.97	0.16	0.20	0.21	0.19	0.22	0.01	0.09	0.01	991	1230	1250	
Maximum	94.48	14.05	12.59	4.43	53.53	4.56	22.18	10.55	4.62	27.58	1472	1605	1620	
1.2. S-MA sub-type														
Mean	45.14	15.79	8.21	5.44	8.04	3.17	6.23	3.17	4.35	0.46	1126	1214	1221	13
Minimum	21.48	9.75	1.60	1.52	0.81	1.10	0.58	0.60	0.16	0.06	914	1100	1100	
Maximum	66.85	23.92	18.53	18.07	15.12	4.77	15.70	11.66	26.20	1.60	1236	1303	1328	
2. C type														
Mean	18.36	50.09	8.34	2.80	4.57	6.71	3.59	3.33	1.82	0.40	1314	1420	1431	22
Minimum	1.86	24.80	0.23	0.77	0.12	2.00	0.37	0.74	0.22	0.10	1100	1195	1210	
Maximum	40.80	83.46	18.73	5.05	14.54	14.57	18.40	14.74	4.84	1.90	1565	1574	1576	
2.1. C-MA sub-type														
Mean	35.04	26.70	7.62	2.46	9.25	4.73	8.47	3.60	1.30	0.84	1208	1221	1230	6
Minimum	27.70	24.80	0.23	0.77	3.90	2.00	2.00	0.83	0.44	0.10	1180	1195	1210	
Maximum	40.80	30.68	13.45	3.84	14.54	6.45	18.40	10.40	2.57	1.90	1236	1246	1249	
2.2. C-LA sub-type														
Mean	12.10	58.86	8.61	2.92	2.82	7.45	1.76	3.23	2.02	0.24	1329	1447	1458	16
Minimum	1.86	37.35	2.60	0.79	0.12	2.33	0.37	0.74	0.22	0.10	1100	1250	1275	
Maximum	26.17	83.46	18.73	5.05	8.94	14.57	3.83	14.74	4.84	1.20	1565	1574	1576	
3. K type														
Mean	25.35	11.79	34.42	8.02	3.11	5.77	3.79	4.33	3.29	0.13	941	1185	1234	25
Minimum	1.65	2.98	8.89	1.90	0.11	1.67	0.53	0.41	0.12	0.01	700	975	1000	
Maximum	57.14	20.95	63.90	31.06	8.75	13.51	36.27	25.74	29.82	0.39	1260	1395	1400	
3.1. K-MA sub-type														
Mean	40.94	9.49	23.15	5.41	2.07	3.40	6.38	3.79	5.22	0.15	879	1080	1172	8
Minimum	8.43	2.98	8.89	2.74	0.67	1.67	0.53	2.22	0.47	0.03	700	975	1025	
Maximum	57.14	15.10	32.16	12.10	5.02	5.83	36.27	5.17	29.82	0.35	1074	1168	1240	
3.2. K-LA sub-type														
Mean	18.02	12.87	39.73	9.25	3.59	6.88	2.57	4.59	2.38	0.12	979	1242	1268	17
Minimum	1.65	4.09	15.35	1.90	0.11	1.96	0.67	0.41	0.12	0.01	775	1000	1000	
Maximum	38.59	20.95	63.90	31.06	8.75	13.51	9.23	25.74	19.88	0.39	1260	1395	1400	
4. CK type, CK-LA sub-type														
Mean	7.37	37.03	25.36	11.06	2.81	8.58	1.30	4.32	2.03	0.14	1173	1298	1333	13
Minimum	0.02	20.03	3.16	3.89	0.10	1.38	0.25	2.22	0.35	0.01	877	1140	1241	
Maximum	12.60	56.85	39.65	40.94	8.74	16.21	2.95	9.70	6.41	0.50	1453	1528	1550	

mean about 54%) because it does not play significant to major roles in every biomass combustion product. In comparison with coal ashes, there are BAs within medium acid and especially low acid types and sub-types (Tables 1 and 2, and Fig. 2) where Si and silicates play, respectively, subordinate to almost insignificant roles in contrast to other mineral classes during ash formation. Despite that, Si is still a leading element even for BAs and their classification because the content of SiO_2 has the greatest variability in the system [1]. Additionally, Si has primary importance for: (1) the specification of types and particularly sub-types; (2) the ash fusion, melt viscosity and activity; and (3) dominant formation of silicates or oxides and their respective glasses in the BA system. It is well known that carbonates, phosphates, sulphates and chlorides transform mostly to oxides and melts with increasing combustion temperatures of biomass [5] and they can react or not with Si if is available in the system. Finally, the ash formation mechanisms in silicate systems such as coal ashes and BAs with high and, to some extent, medium acid tendencies (Fig. 2) are relatively well known ([6–8,68,73] and references therein), whereas the above issue related to BAs with low acid and partially medium acid tendencies is still a relatively unexplored field of investigation.

3.3.3. Ash types

3.3.3.1. "S" type. The "S" ash type consists of BAs belonging to two sub-types with both high ("S-HA") and medium ("S-MA") acid tendencies (Fig. 2). This type includes 27 biomass varieties (31%) from totally 87 fitting to diverse biomass groups and sub-groups [1]. For example, the "S-HA" sub-type comprises biomass varieties from different groups, but mainly from herbaceous and agricultural biomass (coconut shells, palm fibres–husks, reed canary grass, rice husks, rice straw, sorghastrum grass, sugar cane bagasse), to a lesser extent, wood and woody biomass (land clearing wood, pine chips, wood residue) and contaminated biomass (currency shredded, furniture waste, mixed waste paper), and rarely biomass mixtures (wood–straw residue) [1]. On the other hand, the "S-MA" sub-type includes biomass varieties mostly from herbaceous and agricultural biomass group (corn straw, olive husks, olive pits, sweet sorghum grass, switchgrass), and, to a lesser extent, from groups of contaminated biomass (demolition wood, sewage sludge, wood yard waste), wood and woody biomass (Christmas trees, oak wood, spruce wood) and biomass mixtures (biomass mixture, wood–almond residue) [1].

According to the mean contents of ten oxides (Table 9), their order in decreasing values for the specified BA type and sub-types are:

Table 10
Contents (wt.%) of inorganic phases and minerals identified by XRD in rice husk ("S" type, "S-HA" sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	HTA-1500	Mean
1. Inorganic amorphous matter		83	84	30	41	39	33	51.7
2. Inorganic crystalline matter		17	16	70	59	61	67	48.3
2.1. Silicates		3	7	69	59	61	67	44.3
Cristobalite (Cr)	SiO_2	0	3	52	41	48	56	33.3
Quartz (Q)	SiO_2	3	4	4	8	1	1	3.5
Tridymite (Tr)	SiO_2	0	0	13	10	12	10	7.5
2.2. Sulphates		9	7	0	0	0	0	2.7
Arcanite (Arc)	K_2SO_4	9	7	0	0	0	0	2.7
2.3. Chlorides		5	2	1	0	0	0	1.3
Sylvite (Sy)	KCl	5	2	1	0	0	0	1.3
Total		100	100	100	100	100	100	100.0

- $SiO_2 > CaO > Al_2O_3 > K_2O > Fe_2O_3 > P_2O_5 > Na_2O > MgO > SO_3 > TiO_2$ for "S" type.
- $SiO_2 > Al_2O_3 > CaO > K_2O > Fe_2O_3 > TiO_2 > MgO > SO_3 > Na_2O > P_2O_5$ for "S-HA" sub-type.
- $SiO_2 > CaO > K_2O > Al_2O_3 > Fe_2O_3 > P_2O_5 > Na_2O > MgO = SO_3 > TiO_2$ for "S-MA" sub-type.

Hence, Si, Ca, Al, K, Fe, P and Ti oxides are usually the most abundant chemical components in these BAs and the bearing phases and minerals of the above elements play the most important role during ash formation. Additionally, the "S" type normally shows: (1) higher values of Si, Al, Fe and Ti; and (2) lower values of K, Mg and S; in comparison with other BA types (Table 9). The influence of basic components for this type is strongly ("S-HA" sub-type) or slightly ("S-MA" sub-type) limited. The "S" type normally has medium, and, to a lesser extent, high (more characteristic of "S-HA" sub-type) or low (more typical of "S-MA" sub-type) DT and HT ash fusion temperatures (Figs. 8 and 9). Finally, the characteristic ash fusion mechanisms for this type include:

(1) Higher AFTs with moderate softening–melting range and medium flow-dissolution rate ("S-HA" sub-type).
(2) Lower AFTs with short softening–melting range and high flow-dissolution rate ("S-MA" sub-type).

Two of the samples studied in the present work belong to "S" ash type, namely RH ("S-HA" sub-type) and SG ("S-MA" sub-type) (Fig. 1). Their chemical and phase–mineral composition is given in Tables 2, 10 and 11. It can be seen that the "S" type comprises IAM > silicates > carbonates > sulphates > chlorides (Table 18 and Fig. 10). Silicates, sulphates and chlorides are more characteristic of "S-HA" sub-type, while IAM (mainly glass) and carbonates are more typical of "S-MA" sub-type (Tables 10 and 11). The minerals found in this BA type are mostly newly formed (secondary and tertiary) and generated dominantly from biomass enriched in silicates and, to a lesser extent, other mineral classes with both authigenic and detrital origin [5]. The ash formation mechanism of "S" type during biomass combustion is summarized in Table 19 based on data from the present study (Tables 10, 11 and 18, and [5]). Finally, it should be noted that the observed phase–mineral transformations, ash fusion behaviour and ash formation mechanisms for BAs from "S-HA" and partly "S-MA" sub-types are relatively well known ([6–8,68,73] and references therein) because coal ashes also fit into these chemical areas on the triangle graph (Fig. 2).

3.3.3.2. "C" type. The "C" ash type consists of BAs belonging to two sub-types with both medium ("C-MA") and low ("C-LA") acid tendencies (Fig. 2). This type includes 22 biomass varieties (25%) from totally 87 fitting to diverse biomass groups and sub-groups [1]. For example, the "C-MA" sub-type comprises biomass varieties from different groups, but mainly from herbaceous and agricultural biomass (rape straw, peanut shells) and contaminated biomass (greenhouse-plastic waste, refuse-derived fuel), and, to a lesser extent, from wood and woody biomass (alder-fir sawdust) and biomass mixtures (wood–agricultural residue) [1]. In contrast, the "C-LA" sub-type includes biomass varieties almost entirely from the group of wood and woody biomass (balsam bark, beech bark, birch bark, elm bark, eucalyptus bark, hemlock bark, maple bark, pine bark, poplar bark, spruce bark and tamarack bark, as well as forest residue, poplar, sawdust and wood) and only one sample from the group of herbaceous and agricultural biomass (mustard husks) [1]. Therefore, there is a very strong grouping of wood and woody biomass varieties to the C-LA" sub-type.

According to the mean contents of ten oxides (Table 9), their order in decreasing values for the specified BA type and sub-types are:

- $CaO > SiO_2 > K_2O > MgO > Al_2O_3 > Fe_2O_3 > SO_3 > P_2O_5 > Na_2O > TiO_2$ for "C" type.
- $SiO_2 > CaO > Al_2O_3 > Fe_2O_3 > K_2O > MgO > SO_3 > P_2O_5 > Na_2O > TiO_2$ for "C-MA" sub-type.
- $CaO > SiO_2 > K_2O > MgO > SO_3 > P_2O_5 > Al_2O_3 > Na_2O > Fe_2O_3 > TiO_2$ for "C-LA" sub-type.

Hence, Ca, Si, K, Mg, Al, Fe, S and P oxides are usually the most abundant chemical components in these BAs and the bearing phases and minerals of the above elements play the most important role during ash formation. Additionally, the "C" type normally shows: (1) higher values of Ca; and (2) lower values of P and Na in comparison with other BA types (Table 9). The influence of basic components for this type is strongly ("C-LA" sub-type) or slightly ("C-MA" sub-type) enhanced. The "C" type has medium ("C-MA" sub-type) or high and medium ("C-LA" sub-type) DT and HT ash fusion temperatures (Figs. 8 and 9). Finally, the characteristic ash fusion mechanisms for this type include:

(1) Medium AFTs with short softening–melting range and high flow-dissolution rate ("C-MA" sub-type).
(2) Higher AFTs with moderate softening–melting range and high flow-dissolution rate ("C-LA" sub-type).

Only one of the samples studied in the present work belongs to "C" ash type, namely BC from "C-LA" sub-type (Fig. 1). However, it should be noted that many of the municipal solid wastes and refuse-derived fuels, as well as some low rank coals fit in "C-MA" sub-type and the composition, phase–mineral transformations, ash fusion behaviour and ash formation mechanisms for these BAs and coal ashes (Fig. 2) are relatively well known

Table 11
Contents (wt.%) of inorganic phases and minerals identified by XRD in switchgrass (“S” type, “S-MA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	Mean
1. Inorganic amorphous matter		65	65	53	73	64.0
2. Inorganic crystalline matter		35	35	47	27	36.0
2.1. Silicates		13	25	43	25	26.5
Cristobalite (Cr)	SiO_2	0	0	14	0	3.5
Kalsilite (Ks)	$KAlSiO_4$	0	7	7	9	5.8
Leucite (Le)	$KAlSi_2O_6$	7	9	13	12	10.2
Quartz (Q)	SiO_2	6	9	9	4	7.0
2.2. Sulphates		2	2	4	2	2.5
Anhydrite (A)	$CaSO_4$	2	2	4	2	2.5
2.3. Carbonates		20	8	0	0	7.0
Calcite (Cc)	$CaCO_3$	20	8	0	0	7.0
Total		100	100	100	100	100.0

Table 12
Contents (wt.%) of inorganic phases and minerals identified by XRD in beech wood chip (“C” type, “C-LA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	Mean
1. Inorganic amorphous matter		32	45	35	41	100	50.6
2. Inorganic crystalline matter		68	55	65	59	0	49.4
2.1. Silicates		2	0	0	0	0	0.4
Quartz (Q)	SiO_2	2	0	0	0	0	0.4
2.2. Oxydes and hydroxides		0	9	25	36	0	14.0
Lime (L)	CaO	0	0	0	2	0	0.4
Periclase (Peri)	MgO	0	4	3	9	0	3.2
Portlandite (Port)	$Ca(OH)_2$	0	5	22	25	0	10.4
2.3. Phosphates		10	5	12	9	0	7.2
Apatite (Ap)	$Ca(PO_4)_3(Cl,F,OH,CO_3)$	0	0	5	9	0	2.8
Whitlockite (Wl)	$Ca_3(PO_4)_2$	10	5	7	0	0	4.4
2.4. Carbonates		56	41	28	14	0	27.8
Calcite (Cc)	$CaCO_3$	56	41	28	14	0	27.8
Total		100	100	100	100	100	100.0

Table 13
Contents (wt.%) of inorganic phases and minerals identified by XRD in corn cob (“K” type, “K-LA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	Mean
1. Inorganic amorphous matter		45	60	59	74	59.5
2. Inorganic crystalline matter		55	40	41	26	40.5
2.1. Silicates		10	20	27	17	18.5
Kalsilite (Ks)	$KAlSiO_4$	5	6	7	7	6.2
Leucite (Le)	$KAlSi_2O_6$	3	7	6	7	5.8
Quartz (Q)	SiO_2	2	7	14	3	6.5
2.2. Sulphates		2	2	3	0	1.7
Anhydrite (A)	$CaSO_4$	2	2	3	0	1.7
2.3. Carbonates		40	18	11	9	19.5
Kalicinite (K)	$KHCO_3$	40	18	11	9	19.5
2.4. Chlorides		3	0	0	0	0.8
Sylvite (Sy)	KCl	3	0	0	0	0.8
Total		100	100	100	100	100.0

([6–8,68,73–75] and references therein). For example, the occurrence and formation of different silicates (quartz, cristobalite, zeolites, feldspars, wollastonite, vermiculite and sepiolite), oxyhydroxides (portlandite, brucite, magnetite, hematite, rutile, corundum and spinel), sulphates (gypsum, anhydrite and barite), chlorides (halite and hydrophilite), carbonates (calcite, dolomite and ankerite), phosphates (apatite), glass and others in refuse-derived fuel ashes from this “C-MA” sub-type have been characterized [73–75]. The chemical and phase–mineral composition of BC ash is given in Tables 2 and 12. It can be seen that the “C” type comprises IAM > carbonates > oxyhydroxides > phosphates > silicates (Table 18 and Fig. 10). The minerals found in this BA type are mostly newly formed (secondary and tertiary) and generated from biomass enriched in different mineral classes dominantly with authigenic and limited detrital origin [5]. The ash formation mechanism of “C” type during biomass combustion is summarized in Table 19 based on data from the present study (Tables 12 and 18, and [5]).

3.3.3.3. “K” type. The “K” ash type consists of BAs belonging to two sub-types with both medium (“K-MA”) and low (“K-LA”) acid tendencies (Fig. 2). This type includes 25 biomass varieties (29%) from

Table 14
Contents (wt.%) of inorganic phases and minerals identified by XRD in marine macroalgae (“K” type, “K-LA” sub-type) biomass high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	Mean
1. Inorganic amorphous matter		42	24	51	68	100	57.0
2. Inorganic crystalline matter		58	76	49	32	0	43.0
2.1. Silicates		1	2	2	0	0	1.0
Quartz (Q)	SiO_2	1	2	2	0	0	1.0
2.2. Oxides and hydroxides		7	19	10	1	0	7.4
Lime (L)	CaO	0	2	1	1	0	0.8
Portlandite (Port)	$Ca(OH)_2$	7	17	9	0	0	6.6
2.3. Sulphates		11	20	18	31	0	16.0
Anhydrite (A)	$CaSO_4$	11	20	18	31	0	16.0
2.4. Carbonates		19	5	0	0	0	4.8
Calcite (Cc)	$CaCO_3$	19	5	0	0	0	4.8
2.5. Chlorides		20	30	19	0	0	13.8
Halite (Ha)	$NaCl$	18	26	17	0	0	12.2
Sylvite (Sy)	KCl	2	4	2	0	0	1.6
Total		100	100	100	100	100	100.0

Table 15
Contents (wt.%) of inorganic phases and minerals identified by XRD in sunflower shell (“K” type, “K-LA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	Mean
1. Inorganic amorphous matter		44	42	38	34	91	49.8
2. Inorganic crystalline matter		56	58	62	66	9[a]	50.2
2.1. Silicates		0	0	0	0	9[a]	1.8
Leucite (Le)	$KAlSi_2O_6$	0	0	0	0	9[a]	1.8
2.2. Oxides and hydroxides		3	3	14	18	0	7.6
Lime (L)	CaO	0	0	2	2	0	0.8
Periclase (Peri)	MgO	3	3	12	16	0	6.8
2.3. Phosphates		0	4	3	5	0	2.4
Apatite (Ap)	$Ca(PO_4)_3(Cl,F,OH,CO_3)$	0	4	3	5	0	2.4
2.4. Sulphates		30	31	35	43	0	27.8
Anhydrite (A)	$CaSO_4$	2	2	2	0	0	1.2
Arcanite (Arc)	K_2SO_4	28	29	33	43	0	26.6
2.5. Carbonates		23	20	10	0	0	10.6
Fairchildite (F)	$K_2Ca(CO_3)_2$	10	4	3	0	0	3.4
Calcite (Cc)	$CaCO_3$	8	7	0	0	0	3.0
Kalicinite (K)	$KHCO_3$	5	9	7	0	0	4.2
Total		100	100	100	100	100	100.0

[a] The occurrence of leucite is probably a result of contamination from the broken ceramic crucible.

Table 16
Contents (wt.%) of inorganic phases and minerals identified by XRD in plum pit (“CK” type, “CK-LA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	Mean
1. Inorganic amorphous matter		32	31	27	29	100	43.8
2. Inorganic crystalline matter		68	69	73	71	0	56.2
2.1. Silicates		7	13	3	7	0	6.0
Plagioclases (Pl)	$NaAlSi_3O_8–CaAl_2Si_2O_8$	0	0	0	4	0	0.8
Quartz (Q)	SiO_2	7	13	3	3	0	5.2
2.2. Oxides and hydroxides		0	0	10	7	0	3.4
Lime (L)	CaO	0	0	5	0	0	1.0
Periclase (Peri)	MgO	0	0	0	7	0	1.4
Portlandite (Port)	$Ca(OH)_2$	0	0	5	0	0	1.0
2.3. Phosphates		5	16	43	54	0	23.6
Apatite (Ap)	$Ca(PO_4)_3(Cl,F,OH,CO_3)$	5	16	43	54	0	23.6
2.4. Sulphates		2	4	8	3	0	3.4
Anhydrite (A)	$CaSO_4$	2	4	8	3	0	3.4
2.5. Carbonates		54	36	9	0	0	19.8
Fairchildite (F)	$K_2Ca(CO_3)_2$	2	3	2	0	0	1.4
Calcite (Cc)	$CaCO_3$	52	33	7	0	0	18.4
Total		100	100	100	100	100	100.0

Table 17
Contents (wt.%) of inorganic phases and minerals identified by XRD in walnut shell (“CK” type, “CK-LA” sub-type) high-temperature ashes (HTAs) produced at different combustion temperatures (°C).

Phase, mineral	Formula	HTA-500	HTA-700	HTA-900	HTA-1100	HTA-1300	Mean
1. Inorganic amorphous matter		39	35	47	39	47	41.4
2. Inorganic crystalline matter		61	65	53	61	53	58.6
2.1. Oxides and hydroxides		0	0	9	28	21	11.6
Portlandite (Port)	$Ca(OH)_2$	0	0	9	28	21	11.6
2.2. Phosphates		0	0	0	8	10	3.6
Apatite (Ap)	$Ca(PO_4)_3(Cl,F,OH,CO_3)$	0	0	0	8	10	3.6
2.3. Sulphates		2	2	2	0	0	1.2
Anhydrite (A)	$CaSO_4$	2	2	2	0	0	1.2
2.4. Carbonates		59	63	42	25	22	42.2
Butschliite (Bu)	$K_2Ca(CO_3)_2$	11	13	11	0	0	7.0
Fairchildite (F)	$K_2Ca(CO_3)_2$	26	29	0	0	0	11.0
Calcite (Cc)	$CaCO_3$	18	15	27	25	22	21.4
Kalicinite (K)	$KHCO_3$	4	6	4	0	0	2.8
Total		100	100	100	100	100	100.0

Table 18
Mean contents (wt.%) of mineral classes, inorganic phases and minerals for “S”, “C”, “K” and “CK” ash types based on data of eight biomass high-temperature ashes (HTAs) produced at different combustion temperatures (500–1500 °C).

Phase, mineral	Formula	S type	C type	K type	CK type	Four types
1. Inorganic amorphous matter		57.8	50.6	55.4	42.6	51.6
2. Inorganic crystalline matter		42.2	49.4	44.6	57.4	48.4
2.1. Silicates		35.4	0.4	7.1	3.0	11.5
Cristobalite (Cr)	SiO_2	18.4	0	0	0	4.6
Kalsilite (Ks)	$KAlSiO_4$	2.9	0	2.1	0	1.2
Leucite (Le)	$KAlSi_2O_6$	5.1	0	2.5	0	1.9
Plagioclases (Pl)	$NaAlSi_3O_8$–$CaAl_2Si_2O_8$	0	0	0	0.4	0.1
Quartz (Q)	SiO_2	5.2	0.4	2.5	2.6	2.7
Tridymite (Tr)	SiO_2	3.8	0	0	0	1.0
2.2. Oxides and hydroxides		0	14.0	5.0	7.5	6.6
Lime (L)	CaO	0	0.4	0.5	0.5	0.4
Periclase (Peri)	MgO	0	3.2	2.3	0.7	1.5
Portlandite (Port)	$Ca(OH)_2$	0	10.4	2.2	6.3	4.7
2.3. Phosphates		0	7.2	0.8	13.6	5.4
Apatite (Ap)	$Ca(PO_4)_3(Cl,F,OH,CO_3)$	0	2.8	0.8	13.6	4.3
Whitlockite (Wl)	$Ca_3(PO_4)_2$	0	4.4	0	0	1.1
2.4. Sulphates		2.6	0	15.2	2.3	5.0
Anhydrite (A)	$CaSO_4$	1.3	0	6.3	2.3	2.4
Arcanite (Arc)	K_2SO_4	1.3	0	8.9	0	2.6
2.5. Carbonates		3.5	27.8	11.6	31.0	18.5
Butschliite (Bu)	$K_2Ca(CO_3)_2$	0	0	0	3.5	0.9
Fairchildite (F)	$K_2Ca(CO_3)_2$	0	0	1.1	6.2	1.8
Calcite (Cc)	$CaCO_3$	3.5	27.8	2.6	19.9	13.5
Kalicinite (K)	$KHCO_3$	0	0	7.9	1.4	2.3
2.6. Chlorides		0.7	0	4.9	0	1.4
Halite (Ha)	NaCl	0	0	4.1	0	1.0
Sylvite (Sy)	KCl	0.7	0	0.8	0	0.4
Total		100.0	100.0	100.0	100.0	100.0

totally 87 fitting to different biomass groups and sub-groups [1]. For example, the “K-MA” sub-type comprises biomass varieties mostly from the group of herbaceous and agricultural biomass, particularly straw and grass sub-groups (arundo grass, miscanthus grass, barley straw, oat straw, straw, wheat straw, pistachio shells) and rarely from wood and woody biomass group (fir mill residue) [1]. On the other hand, the “K-LA” sub-type includes biomass varieties almost entirely from the group of herbaceous and agricultural biomass (bamboo whole, bana grass, buffalo gourd grass, mint straw, almond hulls, almond shells, hazelnut shells, coffee husks, cotton husks, olive residue, palm kernels, pepper residue, plum pits, sunflower husks, walnut shells) and occasionally from the groups of wood and woody biomass (oak sawdust) and aquatic biomass (algae) [1]. Therefore, there is a relatively strong grouping of biomass varieties, namely herbaceous and agricultural straws and grasses mostly to the “K-MA” sub-type and herbaceous and agricultural residues mainly to the “K-LA” sub-type.

According to the mean contents of ten oxides (Table 9), their order in decreasing values for the specified BA type and sub-types are:

- $K_2O > SiO_2 > CaO > P_2O_5 > MgO > SO_3 > Fe_2O_3 > Na_2O > Al_2O_3 > TiO_2$ for “K” type.
- $SiO_2 > K_2O > CaO > Fe_2O_3 > P_2O_5 > Na_2O > SO_3 > MgO > Al_2O_3 > TiO_2$ for “K-MA” sub-type.
- $K_2O > SiO_2 > CaO > P_2O_5 > MgO > SO_3 > Al_2O_3 > Fe_2O_3 > Na_2O > TiO_2$ for “K-LA” sub-type.

Hence, K, Si, Ca, P, Mg, S, Fe and Na oxides are usually the most abundant chemical components in these BAs and the bearing phases and minerals of the above elements play the most important role

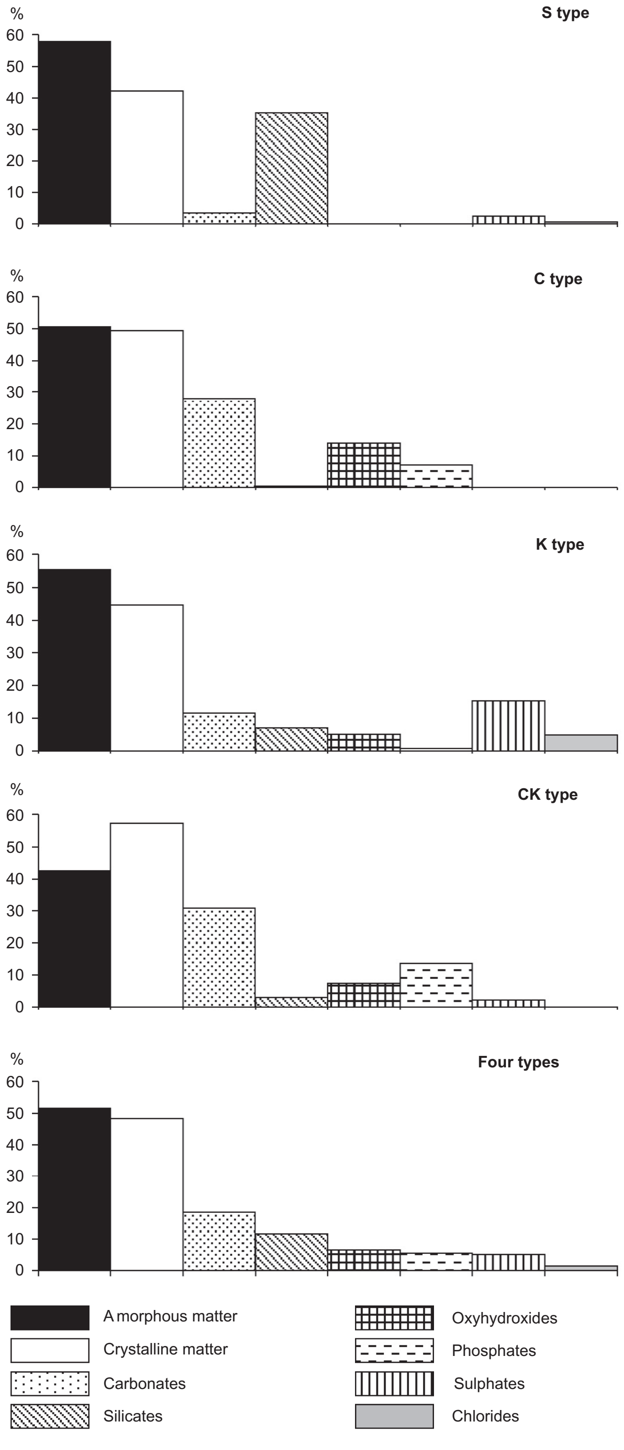

Fig. 10. Mean distribution of amorphous matter, crystalline matter and mineral classes in biomass ash types based on eight biomass ashes produced at 500, 700, 900, 1100, 1300 and 1500 °C, wt.%.

during ash formation. Additionally, the "K" type normally shows: (1) higher values of K, S and Na; and (2) lower values of Ca and Ti in comparison with other BA types (Table 9). The influence of basic components for this type is strongly ("K-LA" sub-type) or slightly ("K-MA" sub-type) enhanced. The "K" type has low (commonly lower for "K-MA" than "K-LA") to medium (normally higher for "K-LA" than "K-MA") DT and HT ash fusion temperatures (Figs. 8 and 9). Finally, the characteristic ash fusion mechanisms for this type include:

(1) Lower AFTs with large softening–melting range and slow flow-dissolution rate ("K-MA" sub-type).
(2) Lower AFTs with large softening–melting range and medium flow-dissolution rate ("K-LA" sub-type).

Three of the samples studied in the present work belong to "K" ash type, namely CC, MM and SS from "K-LA" sub-type, as CC is almost at the border between "K-LA" and "K-MA" sub-types, while MM and SS are nearly to the border between "K-LA" and "CK-LA" sub-types (Fig. 1). There is no sample from "K-MA" sub-type; however, it is obvious that the composition, phase–mineral transformations, ash fusion behaviour and ash formation mechanisms for this sub-type could be intermediate between SG sample ("S-MA") and CC sample ("K-LA"), which are close to the borders of K-MA sub-type. The chemical and phase–mineral composition of CC, MM and SS is given in Tables 2 and 13–15. It can be seen that the "K" type comprises IAM > sulphates > carbonates > silicates > oxyhydroxides > chlorides > phosphates (Table 18 and Fig. 10). The minerals found in this BA type are mostly newly formed (secondary and tertiary) and generated from biomass enriched in different mineral classes dominantly with authigenic and limited detrital origin [5]. The ash formation mechanism of "K" type during biomass combustion is summarized in Table 19 based on data from the present study (Tables 13–15 and 18, and [5]),

3.3.3.4. "CK" type. The "CK" ash type is analogous to "CK-LA" sub-type and consists of BAs belonging only to low acid tendency (Fig. 2). This type includes 13 biomass varieties (15%) from totally 87 fitting to different biomass groups and sub-groups. It comprises biomass varieties mainly from the group of herbaceous and agricultural biomass (kenaf grass, alfalfa straw, grape marc, pepper plant, soya husks, walnut blows, walnut hulls-blows), and to a lesser extent, wood and woody biomass (olive wood, pine pruning, pine sawdust, willow) and animal biomass (chicken litter, meat-bone meal) [1]. Therefore, there is some characteristic grouping of biomass varieties in this type, especially for animal biomass and certain herbaceous–agricultural and wood–woody assortments.

According to the mean contents of ten oxides (Table 9), their order in decreasing values for the specified BA type is:

- $CaO > K_2O > P_2O_5 > MgO > SiO_2 > SO_3 > Al_2O_3 > Na_2O > Fe_2O_3 > TiO_2$.

Hence, Ca, K, P, Mg, Si and S oxides are usually the most abundant chemical components in these BAs and the bearing phases and minerals of the above elements play the most important role during ash formation. Additionally, the "CK" type normally shows: (1) higher values of P and Mg; and (2) lower values of Si, Al and Fe in comparison with other BA types (Table 9). The influence of basic components for this type is strongly enhanced. The "CK" type has medium, and to a lesser extent high and low DT and HT ash fusion temperatures (Figs. 8 and 9). Finally, the characteristic ash fusion mechanism for this type includes:

- Different AFTs with moderate softening–melting range and medium flow-dissolution rate.

Hence, this type normally shows intermediate characteristics between the "K-LA" and "C-LA" sub-types.

Two of the samples studied in the present work belong to "CK" ash type, namely PP and WS, as MM and SS samples are close to the border between "CK" type and "K-LA" sub-type (Fig. 1). The chemical and phase–mineral composition of PP and WS is given in Tables 2, 16 and 17. It can be seen that the "CK" type comprises IAM > carbonates > phosphates > oxyhydroxides > silicates > sulphates

Table 19
Ash formation mechanisms for "S", "C", "K" and "CK" ash types based on data of eight biomass high-temperature ashes (HTAs) produced at different combustion temperatures (500–1500 °C).

Process	S type	C type	K type	CK type
1. Sequential phase–mineral transformations in biomass ashes with increasing combustion temperatures	1.1. Initial formation of intermediate and less stable chlorides (sylvite), carbonates (calcite), sulphates (anhydrite, arcanite) and inorganic amorphous (non-glass) material	1.1. Initial formation of intermediate and less stable carbonates (calcite), hydroxides (portlandite), phosphates (whitlockite) and inorganic amorphous (non-glass) material	1.1. Initial formation of intermediate and less stable chlorides (halite, sylvite), hydroxides (portlandite), carbonates (K carbonate, calcite, fairchildite), sulphates (arcanite, anhydrite) and inorganic amorphous (non-glass) material	1.1. Initial formation of intermediate and less stable hydroxides (portlandite), carbonates (calcite, fairchildite, butschliite, K carbonate), sulphates (anhydrite) and inorganic amorphous (non-glass) material
	1.2. Subsequent generation of more stable silicates (cristobalite, quartz, tridymite, leucite, kalsilite)	1.2. Subsequent generation of more stable oxides (periclase, lime), phosphates (apatite) and silicates (quartz)	1.2. Subsequent generation of more stable oxides (periclase, lime), phosphates (apatite) and silicates (quartz, leucite, kalsilite)	1.2. Subsequent generation of more stable oxides (periclase, lime), phosphates (apatite) and silicates (quartz, plagioclases)
	1.3. Softening and melting (especially for S-HA sub-type) accompanied by dissolution of the refractory minerals (particularly for S-MA sub-type) by less (S-HA sub-type) or more active (S-MA sub-type) melts	1.3. Softening and melting accompanied by high dissolution of the refractory minerals by more active melts	1.3. Softening and melting accompanied by dissolution of the refractory minerals by less or more active melts	1.3. Softening and melting accompanied by dissolution of the refractory minerals by medium active melts
2. Final crystallizations and glass formation during cooling of biomass ashes	Crystallization of the above silicates in melt and formation of glass accompanied by limited salt condensation and hydroxylation, hydration and carbonation of newly formed phases	Crystallization of melt and formation of glass accompanied by significant salt condensation and intensive carbonation, hydroxylation and hydration of newly formed phases	Crystallization of the above silicates in melt and formation of glass accompanied by extensive salt condensation and intensive carbonation, hydroxylation and hydration of newly formed phases	Crystallization of the above silicates in melt and formation of glass accompanied by extensive salt condensation and intensive carbonation, hydroxylation and hydration of newly formed phases
3. Post-combustion transformations through storage of biomass ashes	Some quite limited transformations of the newly formed minerals and phases to stable species during weathering (tertiary) among carbonates (calcite) due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air	Some extensive transformations of the newly formed minerals and phases to stable species during weathering (tertiary) among carbonates (calcite) and hydroxides (portlandite) due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air	Some extensive transformations of the newly formed minerals and phases to stable species during weathering (tertiary) among hydroxides (portlandite) and carbonates (kalicinite, calcite, fairchildite) due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air	Some extensive transformations of the newly formed minerals and phases to stable species during weathering (tertiary) among hydroxides (portlandite) and carbonates (calcite, fairchildite, butschliite, kalicinite) due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air

(Table 18 and Fig. 10). The minerals found in this BA type are mostly newly formed (secondary and tertiary) and generated from biomass enriched in different mineral classes with authigenic and quite limited detrital origin [5]. The ash formation mechanism of "CK" type during biomass combustion is summarized in Table 19 based on data from the present study (Tables 16–18 and [5]),

Finally, the above observations show that IM of biomass varieties has variable performance during combustion; however, the present study clearly reveal that the thermal behaviour of IM, ash fusion and ash formation mechanisms of different BAs tend to be relatively: (1) diverse between the inorganic "S", "C", "K" and "CK" types; and (2) similar within the inorganic types and especially sub-types specified; despite some exceptions. It should be noted that the evaluation of morphological characteristics of different BA types and sub-types with increasing combustion temperatures will be reported in a future publication.

3.4. Potential applications of ash formation mechanisms for biomass types and sub-types

The potential utilization, technological and ecological advantages and challenges connected with biomass and particularly BAs specified in different chemical types and sub-types have been characterized in detail recently [4]. Numerous aspects related to innovative and sustainable utilization of BA such as: (1) bulk utilization (for soil amendment and fertilization; production of construction materials, adsorbents, ceramics and other materials; plus synthesis of minerals); (2) recovery of valuable components and their utilization (char, water-soluble, cenosphere–plerosphere, magnetic and heavy fractions; and elements); and (3) multicomponent utilization; have been described therein [4]. Additional issues connected with BAs, namely: (1) technological advantages and challenges (slagging, fouling and corrosion; low ash-fusion temperatures; erosion and abrasion; co-combustion and co-gasification; prediction of phase composition; and others); and (2) some environmental risks and potential health concerns (air, water, soil and plant contamination; acidity, alkalinity and leaching; volatilization, retention, capture and immobilisation of hazardous elements and compounds; ash inhalation and disposal); during biomass and BA processing have been also discussed therein [4]. Therefore, only some key technological and environmental topics related to the phase–mineral transformations, ash fusion behaviour and ash formation mechanisms of biomass types and sub-types during combustion will be discussed herein based mostly on the mineralogical data obtained for eight biomass varieties (Tables 10–18 and [5]).

3.4.1. Technological problems

3.4.1.1. Fusion, slagging, fouling and other predictions. The reference investigations show that threshold values of numerous simple or more complex indexes (or indices) and indicators based on chemical composition of BA have been used for predicting the ash fusion, slagging, deposit formation, fouling, agglomeration, sintering or corrosion problems during thermo-chemical conversion of biomass. Such indexes are currently the most commonly used approach among others for an evaluation of the above problems. These indexes include contents, sums and/or ratios of:

- CaO/K_2O, Fe_2O_3/CaO, SiO_2/Al_2O_3 and SiO_2/K_2O.
- $K_2O + Na_2O$ plus heating value (alkali index).
- Cl and S contents and their ratio.
- $Cl/(K + Na)$.
- $Fe_2O_3/(K_2O + Na_2O)$ (bed agglomeration index).
- $(K_2O + Na_2O)/SiO_2$ (deposition and fouling index).
- $(K + Na)/(2S + Cl)$ as molar ratios (agglomeration indicator).
- $(CaO + MgO)/(K_2O + Na_2O)$ (agglomeration or sintering index).
- $SiO_2/(SiO_2 + Fe_2O_3 + CaO + MgO)$ (slag viscosity index).
- $(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)/(SiO_2 + Al_2O_3 + TiO_2 \pm P_2O_5)$ (base-to-acid ratio) and occasionally multiplied by the ash content, Na_2O, sum $Na_2O + K_2O$ (fouling index) and S (slagging Babcock index).
- Water-soluble $K_2O + Na_2O + CaO + MgO$ (multi fuel fouling index) and even high ash contents [15,19,32,33,35–38,41,42,44,45,49–51,58,60,61,63,64,76–91].

However, the present study undoubtedly reveals that these chemical indexes can be only preliminary and proximate indicators for such problems. It should be stated that this chemical approach cannot adequately predict or explain the real behaviour of biomass fuels and their conversion products because the leading reasons are modes of element occurrence, namely specific phases and minerals that contain this element. Unfortunately, the creation of the above indexes is based solely on bulk chemical composition of BA and they cannot represent: the fluxing or refractory; active, pozzolanic or inert; volatile or non-volatile; and soluble or insoluble proportions of each element in the biomass or BA systems (see also Sections 3.4.1.2–3.4.1.4 and 3.4.2). For example, Table 8 definitely illustrates that the elements can have dual fluxing (with MPs 1200 °C) or refractory (with MPs >1200 °C) behaviour during thermo-chemical conversion of biomass depending on the bearing phases and minerals of the elements and present in the system. Additionally, it was even supposed that solid biofuels with higher ash contents tend to produce increased ash deposition, slagging, fouling and corrosion problems [44,83]. It is obvious that this statement cannot be universal because some high ash fuels such as rice husks with about 16–19% ash yield (Table 2 and [1]) normally do not create such problems. On the other hand, it should be stated that even ashes with identical chemical composition (it means identical index) and similar mineral composition can occasionally demonstrate different thermal behaviour as a result of some other factors (see Section 3.2.4).

The present study shows that the real behaviour for a biomass fuel during combustion (which is also valid for any thermo-chemical conversion) is directly related to the phase–mineral composition and ash formation mechanism of this specific fuel through processing. Therefore, only a combination of data generated simultaneously from the above chemical and phase investigations can supply enough information to evaluate or predict the actual behaviour of elements during biomass combustion ([5,67,68] and as Figs. 8 and 9). Finally, reliable explanations and predictions of the above mentioned problems in some cases are complicated without considering additional factors. For instance, it has been reasonably stated that the evaluation of slagging, fouling and corrosion problems depends on an understanding of many factors such as origin, particle size, association and behaviour of mineral species (not elemental composition) and their juxtaposition with regard to combustibles, gas environment and temperatures during combustion [11]. Hence, the assignment of biomass varieties to combined chemical and mineral ash types and sub-types (Figs. 1, 2 and 8–10) can supply much better information for the prediction and evaluation of the above problems than chemical indexes.

3.4.1.2. Low ash fusion temperatures. It is widely accepted that most of the serious slagging, deposit formation and fouling problems during biomass combustion results from the low ash melting temperatures [4]. As pointed above (see Section 3.2.4) melt formation in combustion products can initiate at different temperatures depending on the phase composition of biomass and BA. The low ash fusion biomass varieties normally have high slagging propensity due to occurrence of low temperature melts and their subsequent intensive melt crystallization followed by abrupt glass formation during cooling at relatively lower temperatures. On the other hand, biomass varieties with high ash fusion temperatures commonly show lower slagging propensity because their ash fusion temperatures are high and the above processes are less intensive during combustion. For example, the medium to high contents of Si and K in biomass (excluding some highly enriched in Si varieties) greatly contribute to extremely low AFTs. It seems that the combination of such concentrations for Si and K in the BA system (represented mostly as K silicates and inorganic amorphous matter) has a leading role in the formation of some low-temperature eutectics that strongly influence ash fusion behaviour. It has been noted earlier that a mixture of 68% of SiO_2 and 32% K_2O (with a 2.1 ratio) can melt even at 769 °C [78]. The present study shows that contents of SiO_2 and K_2O normally in the range 43–68% and 19–34%, respectively, and with SiO_2/K_2O ratio between 1.3 and 4.0 (mean about 2.1–2.3) for BAs with acid and medium acid tendencies (Figs. 1 and 2) is critical for formation of low-temperature eutectics and active melts that dissolve relatively quickly the residual refractory minerals or phases in the system. It can often be seen that straws and some grasses from “S-MA” and, to a lesser extent, “K-MA” and “S-HA” sub-types belong to these critical positions on the triangle graph (Table 1 and Figs. 1d and 2 and [1]). It is interesting to note that the above SiO_2/K_2O ratios are typical of K-bearing silicate minerals such as kalsilite–kaliophilite (1.3), leucite (2.6), orthoclase, microcline and muscovite (3.8), and to lesser extent sanidine (5.1) and illite (7.4). The present study reveals that kalsilite–kaliophilite and leucite are characteristic minerals in SG (“S-MA” sub-type) and CC (“K-LA” sub-type) HTAs, which belong (SG) or are close (CC) to the medium acid tendency (Fig. 1). Hence, the identification of such K-rich minerals in BAs can be used as an indicator for possible problems related to formation of low-temperature eutectics and very active melts in the system.

The present study also shows that the lower AFTs with short softening–melting range and high flow-dissolution rate (“S-MA” sub-type) seem to be the worst case for slagging and fouling. In contrast, higher AFTs with moderate softening–melting range (“S-HA” and “C-LA” sub-types) and medium (“S-HA” sub-type) or high (“C-LA” sub-type) flow-dissolution rates are the best cases for avoiding such problems.

The reference investigations reveal that a beneficial approach for problematic low ash fusion biofuels or alternative bed materials for fluidized bed combustion is to use additives, namely kaolinite, mullite, clinochlore, bentonite, K feldspar, plagioclase, olivine, quartz, lime, bauxite, gibbsite, diaspore, corundum, hematite, calcite, dolomite, magnesite, ankerite, sand, high alumina sand, limestone, diatomaceous earth, dicalcium phosphate, chalk, elemental S, peat and coal fly ash [17–19,55,78,86,87,92–97]. The application of such additives is to prevent the agglomeration, sintering and slagging tendencies by achieving higher ash melting temperatures. However, there are many solid fuels which are naturally abundant in these refractory minerals and appropriate blending of such fuels can avoid the use of non-fuel and normally expensive additives (see Section 3.4.1.3).

3.4.1.3. Co-combustion. Increasing large-scale combustion of natural biomass and its co-combustion with semi-biomass (contaminated biomass such as municipal solid waste, refuse-derived fuel, sewage sludge, demolition wood and other industrial organic wastes) and solid fossil fuels (coal, peat, petroleum coke) seems to be one of the main drivers for biofuel promotion in many countries worldwide in the near future ([3,4] and references therein). Therefore, phase–mineral transformations, ash fusion behaviour and ash formation mechanisms of biomass types and sub-types during combustion have a crucial importance for such future non-problematic co-combustion and even co-gasification of biomass with coal and other fuels because the fuel mix can play a leading role to solve different technological and ecological problems.

The present study shows that some biomass varieties, mainly from "K-MA", "K-LA" and "S-MA" and partly "CK-LA" and "S-HA" sub-types, are prone to create potentially serious problems during their combustion or co-combustion with coal. It can be seen that such biofuels are located to the right positions on the triangle graph for the above sub-types (Figs. 8 and 9). Hence, the favourable and less problematic future fuel mixtures between biomass, coal and other solid fuels may include an adjustment of chemical composition for fuel blends to fit preferentially closer to "C-LA" and "S-HA" sub-types or at least to "S-MA", "K-MA", "K-LA" and "CK-LA" sub-types, but belonging mostly to the left positions on the triangle graph (Figs. 8 and 9). The above approach could also be applicable for use of better alternative bed materials for fluidized bed combustion of biomass.

Furthermore, it seems that the utilization of lower rank coals, which normally have lower AFTs and are enriched in Ca, Mg, Fe and S and their bearing phases [70]), may be good candidates to mix with most of biomass types and sub-types. On the other hand, it can be supposed that the application of higher rank coals (commonly with higher AFTs and enriched in Si, Al, Ti, K and Na and their bearing phases [70]) could be more favourable to blend mostly with biomass from "C-LA", "S-HA" and "C-MA" sub-types, and to some extent, biomass varieties from other sub-types, but belonging preferentially to the left positions on the triangle graph (Figs. 8 and 9). The purpose of the above blending is to provoke the intensive formation of more refractory minerals (silica minerals, mullite and Ca and Mg silicates, oxides and phosphates) and less fluxing phases (K and Na silicates, chlorides, sulphates and phosphates) in the system (Tables 8 and 10–18). Another interesting perspective is the use of blends including: (1) coals with high AFTs and greatly enriched in kaolinite and Si- and Ti-bearing minerals (for example, higher rank Gondwana coals [69,70]) as a precursor for formation of refractory mullite, cristobalite, tridymite and rutile in the system; and (2) biomass varieties with relatively low to medium contents of K and Na. Finally, such advanced future fuel blends may even have positive effects also on: (1) increasing share of biomass during co-combustion; and (2) some environmental issues related to the depressed volatilization and leaching of hazardous elements and components during biomass co-combustion, respectively (see Section 3.4.2). Hence, the above innovative approaches to biomass combustion and co-combustion are vital for trouble-free fuel processing and the biomass types and sub-types specified have a huge potential for future investigations and advanced applications.

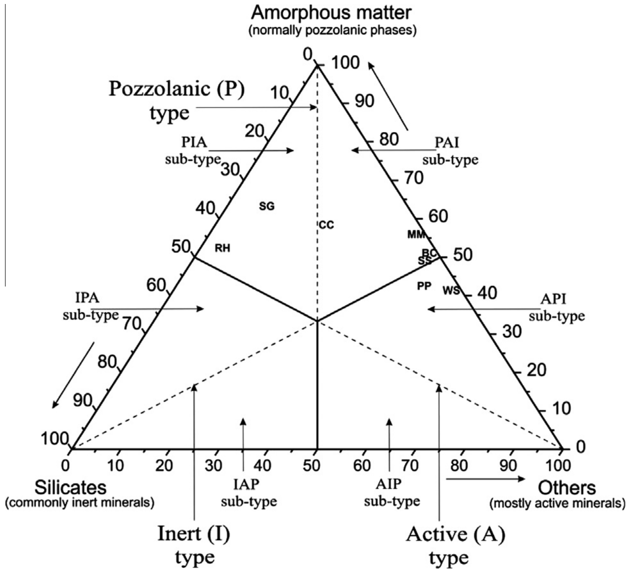

Fig. 11. Positions of eight biomass varieties in the phase–mineral classification of biomass ash, based on their mean contents of amorphous matter, silicates and others (carbonates + oxyhydroxides + phosphates + sulphates + chlorides) for high-temperature ashes produced at 500, 700, 900, 1100, 1300 and 1500 °C, wt.%. Abbreviations: BC, beech wood chips; CC, corn cobs; MM, marine macroalgae; PP, plum pits; RH, rice husks; SG, switchgrass; SS, sunflower shells; WS, walnut shells.

3.4.1.4. Application of biomass ash. The present and former [4,5] studies show that BAs can be enriched in different components as each mineral or phase in BA has individual and/or synergetic:

(1) Active (lime, periclase, anhydrite, bassanite, Ca and Ca–Mg silicates and alumino-silicates, Ca-enriched glass, others) to semi-active (portlandite, brucite, gypsum, carbonates, clay and mica minerals, feldspars, Fe oxides, Ca-containing glass and other sulphates, chlorides and phosphates).
(2) Pozzolanic (glass).
(3) Inert (inactive to less active quartz, cristobalite, tridymite, mullite, other silicates and some char) behaviour; during hydration–dehydration, hydroxylation–dehydroxylation and subsequent carbonation processes of BAs.

The active and semi-active minerals and phases of BAs form reactive substances in water that cause hardening and binder effects in the system during evaporation of water. Such effects are a result of formation of new and relatively stable silicates, alumino-silicates, sulphates, carbonates, hydrates and oxyhydroxides containing water molecules and/or hydroxyl groups. These newly formed crystalline and amorphous products bind the pozzolanic and inert phases relatively quickly in such multicomponent systems. On the other hand, the pozzolanic reactions of BAs are mostly diffusion-controlled processes and they start to work later in the hardening process. The above-mentioned complex processes

Table 20
Mean and range values of elements volatilized during biomass combustion, wt.% (based on [3]).

Element	Mean	Minimum	Maximum	Samples
Hg	99	95	100	5
Cd	95			1
Sb	95			1
Se	95			1
V	95			1
Br	85	80	90	2
Cr	75	70	80	2
Pb	71	40	100	5
Zn	70	3	95	7
Cl	66	15	100	9
As	58	25	90	2
S	57	7	90	15
K	36	5	90	8
Na	13	2	24	2

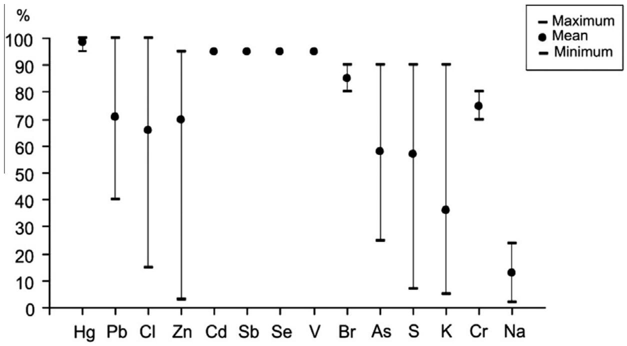

Fig. 12. Mean and range contents of elements volatilized from biomass during combustion, wt.%.

play a leading role in the production of construction materials and some other applications, and the bulk chemical and phase–mineral composition of BA provides vital information for that purpose [4].

The present phase–mineral study confirmed most of the preliminary chemical observations about the potential use of different BA types and sub-types [4]. For example, BA sub-types can exhibit preferably: (1) inert (normally "S-HA"); (2) pozzolanic (commonly "C-MA", "S-MA" and "K-MA"); and (3) active or cementitious (mainly "C-LA", "CK-LA" and K-LA) binding properties from upper to lower areas on the graph for chemical classification of BAs (Fig. 2) and distribution of mineral classes in BA types (Fig. 10). Additionally, it can be seen that BA types can have active, semi-active to inert properties with different tendencies, namely:

- IAM > silicates > carbonates > sulphates > chlorides ("S" type).
- IAM > carbonates > oxyhydroxides > phosphates > silicates ("C" type).
- IAM > sulphates > carbonates > silicates > oxyhydroxides > chlorides > phosphates ("K" type).
- IAM > carbonates > phosphates > oxyhydroxides > silicates > sulphates ("CK" type) (Table 18 and Fig. 10).

Hence, the BA properties and behaviour can be more or less favourable for applications in the building industry, whereas the unfavourable BAs can be more suitable for an alternative use in this or other industries. The observations above are similar to those described for coal ashes [7].

Furthermore, when there are data for phase–mineral composition of BAs it is possible to classify them to types and sub-types with dominant pozzolanic, inert or active properties as the eight biomass varieties in the present study (Fig. 11). The borders used for this phase–mineral classification of BAs are the same applied earlier for classification of biomass by organic structural components (Fig. 1c and [2]). Thus the triangle graph was divided into six sectors labelled ("PIA", "PAI", "IPA", "IAP", "API" and "AIP") in such a way that each point in a given sector is characterized by the consecutive decreasing quantities of the three mineral constituents (amorphous matter, silicates and other minerals). It can be seen (Fig. 11) that BAs studied have dominant pozzolanic-inert (RH and SG from "S" chemical type), pozzolanic-active (CC, MM, BC and SS from "K" and "C" chemical types) or active-pozzolanic (PP and WS from "CK" chemical type) properties based on their mean phase–mineral composition (Tables 10–17). Therefore, there is some relatively good agreement between chemical and phase–mineral classifications of BAs. It is interesting to note that the positions of BAs on the graph (Fig. 11) can be changeable depending on the specific biomass combustion temperatures used (Tables 10–17). Finally, the above phase–mineral classification or similar classifications related to mineral classes, groups or species can also be created and applied for the prediction of different innovative and sustainable utilization of BAs (soil amendment and fertilization, production of construction materials, adsorbents, ceramics, synthesis of minerals, recovery of valuable components and multicomponent utilization), as well as reducing some technological and environmental problems related to BA and described in detail elsewhere [4].

3.4.2. Environmental problems

3.4.2.1. Volatilization and capture of hazardous elements during biomass combustion. Certain results in reference investigations concerning the concentrations of elements such as Ag, As, Ba, Cd, Cl, Cr, Cu, Hg, Mn, Mo, Ni, Pb, S, Sb, Se, Sn, Th, Tl, U, V and Zn in BAs are very disturbing ([4] and references therein). Additionally, these elements tend to occur in much more mobile and hazardous compounds than in coal ash [4]. For example, the variable (mean and range) proportions of elements emitted during biomass combustion are given in Table 20 and Fig. 12. It can be seen that elements such as Hg > (Cd, Sb, Se, V) > Br > Cr > Pb > Zn > Cl > As > S > K > Na demonstrate the highest volatilization potential according to mean values ([3] and references therein). Unfortunately, such volatilized elements present some environmental risk and potential health concern because they could contaminate the air, soil, water and plants in the areas surrounding biomass-fired power plants. Hence, some biomass fuels and their BAs are the basis for potentially serious global and local contamination concerns during future large-scale combustion of biomass.

It is well known that besides biomass composition, combustion temperature has a leading effect on the ash yield, element volatilization and qualitative and quantitative composition of ashes produced from different biomass varieties [3,5]. The present study (Table 2) reveals that the ash yields determined at maximum temperatures (1100–1500 °C) for eight biomass samples are 7–59% lower than those produced at 500 °C, namely MM (59%) > SS (44%) > WS (43%) > BC (39%) > CC (33%) > PP (29%) > SG (19%) > RH (7%). It can be seen that the volatilization decreases in the order: "K" > "C" > "CK" > "S" for BA types and "K-LA" > "C-LA" > "CK-LA" > "S-MA" > "S-HA" for BA sub-types. Therefore, the above orders are very informative and show that the maximum losses are typical for biomass varieties (MM, SS, WS, BC), sub-types (these with low acid tendency) and types abundant commonly in Ca, Cl, K, Mg, Na, P, S, chlorides, sulphates, carbonates and phosphates (Tables 2, 9, 12, 14, 15, 17 and 18, and Figs. 1d, 10 and 11). In contrast, minimum losses occur for biomass types, sub-types (these with medium and especially low acid tendency) and varieties highly (RH, SG) or significantly (CC and PP) enriched in Si, Al, Fe, Ti, amorphous matter and silicates (Tables 2, 9–11, 13, 16 and 18, and Figs. 1d, 10 and 11). These weight losses for biomass are normally higher than for coal and such differences are a result of some more intensive phase transformations (loss of adsorbed and combined water, combustion of volatile matter, decomposition of less stable minerals) and probably higher volatilization behaviour of certain mobile elements (Br, C, Cl, H, Hg, K, N, Se, S and other trace elements) from biomass phases in the higher temperature ranges [3–5].

It is commonly accepted in the reference investigations that the volatile elements are mostly associated with the easily decomposed organic matter and mineral classes such as carbonates, sulphates, chlorides, nitrates and sulphides in biomass, similar to coal ([4] and references therein). Hence, the present study confirmed the earlier presumptions [3–5] that biomass normally with: (1) low ash yield and less acid and detrital tendencies; and (2) high authigenic mineralization; is more prone to such volatilization (particularly "K-LA", "C-LA" and "CK-LA" sub-types in Figs. 1 and 2). In contrast, more limited loss of volatile elements could be expected when they mainly occur in stable minerals in biomass such as silicates, oxides and some phosphates ("S-MA", "C-MA", "K-MA" and especially "S-HA" sub-types in Figs. 1 and 2). However, it should be stated that the behaviour of volatile elements also depends on combustion (plus cleaning) technologies and especially on the composition of combustion residues in power plants (fly ash, bottom ash/slag) that can effectively capture and immobilize such elements, similar to coal ([4] and references therein).

The retention, capture and immobilization of potentially hazardous air pollutant (HAP) elements (Ag, As, Ba, Be, C, Cd, Cl, Co, Cr, Cu, F, Hg, Mn, N, Ni, Pb, S, Sb, Se, Sn, Th, Tl, U, V, Zn, others) and/or some of their compounds (CO, CO_2, CH_4, HCl, Cl_2, HF, NO_X, N_2O, NH_3, SO_X, H_2S, polycyclic aromatic hydrocarbons, polychlorinated dioxins and furans, others) during combustion of biomass and other solid fuels have been discussed earlier ([4] and references therein). Shortly, different original silicates, oxides and some phosphates in biomass do not undergo phase transformations such as decomposition, melting or boiling up to 1200–1500 °C in boilers [4,5]. Hence, typical volatile HAP elements associated with these stable minerals in biomass (particularly "S-HA" and occasionally "S-MA", "C-MA" and "K-MA" sub-types) should remain in the combustion residues and their release with the flue gases and stack emissions is possible only by fine fly ashes that are not-captured. However, many HAP elements can sublimate and/or evaporate in biomass boilers during combustion and some may not be captured by cleaning equipments in power plants. On the other hand, some HAP elements occur as volatile species in the furnaces of power plants and condense and adsorb completely or partially downstream, preferentially on the finer fly ash particles with higher specific surface, as the temperature of the flue gas drops ([4] and the references therein). In this case, the reason for increased capture of volatile HAP elements in fly ash is caused by some minerals or phases with well-known sorbent properties and present in the combustion residue (especially "C-LA", "CK-LA" and "K-LA" sub-types).

The complete or partial capture and immobilisation of the volatile HAP elements can be achieved from some phases originally present in solid fuels and particularly newly formed products from these phases during combustion. For instance, processes such as: (1) hydroxylation (100–600 °C); (2) carbonation (200–500 °C); (3) oxidation (200–700 °C); (4) sulphation (300–1000 °C); (5) char formation (>400 °C); (6) silicate crystallization and recrystallization (>400 °C); and (7) melt/glass formation (>1000 °C); are mainly responsible for the capture and immobilisation of volatile elements by reactions between solid, liquid and gaseous phases in the system. The possible mechanisms for reactions between metal vapours and dispersed substrates have been proposed and described earlier to explain the capture and immobilisation behaviour of the most volatile elements in the ash residues. For that purpose, the important roles of effective sorbents, such as clay minerals, Ca-, Mg-, K-, Na-, Fe- and Al-bearing sulphates, carbonates and oxyhydroxides, char and glass, in the capture and immobilisation of some trace elements have been discussed ([4] and references therein). Therefore, many minerals and phases in biomass and BA can play the above sorbent role because BAs show much more variable composition in contrast to ashes of other solid fuels (Tables 1, 2 and 9–18, Figs. 1, 2, 10 and 11, and [1–5]).

An interesting phenomenon in some power plants using coal, biomass, coal/biomass blends and other solid fuels could be the increased capture and immobilization of some volatile HAP elements (in particular trace elements) in combustion residues. This phenomenon is known as the concept of "self-cleaning fuels" recently developed, where specific mineral classes, groups or species and chars contribute to cleaning process [72]. Shortly, certain solid fuels are highly enriched in: (1) Ca-, K-, Mg- and Na-bearing

Table 21
Mean and range contents of water-soluble elements leached from different biomass varieties and their high-temperature ashes, wt.% (based on [2,3]).

Element	Biomass			Biomass ash			Samples
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	
Cl	87	59	98	68	8	99	17
K	71	25	93	44	2	98	26
Na	60	18	96	36	0	100	22
P	51	4	97	2	0	15	15
S	46	15	100	58	16	97	14
N	37						
Mg	36	7	68	4	0	39	17
Mn	23			10	0	46	7
Al	9	0	40	1	0	9	13
Ca	7	3	15	3	0	20	19
Fe	4	0	12	1	0	1	14
Si	2	0	5	6	0	74	13
As	Trace			0			1
Ba	Trace			3			1
Co	Trace			8	0	15	4
Cu	Trace			3	0	10	8
Mo	Trace			6	Trace	12	2
Pb	Trace			4	Trace	15	5
Sr	Trace			15			1
Ti	Trace			0			12
V	Trace			0			1
Zn	Trace			8	0	44	8
Ni				10	0	18	4
Cd				8	0	49	6
Cr				8	0	30	5
Li				5			1
Se				2			1
Sb				1	Trace	1	2
Br				Trace			1
Hg				Trace			1
B				0			1
Sn				0			1

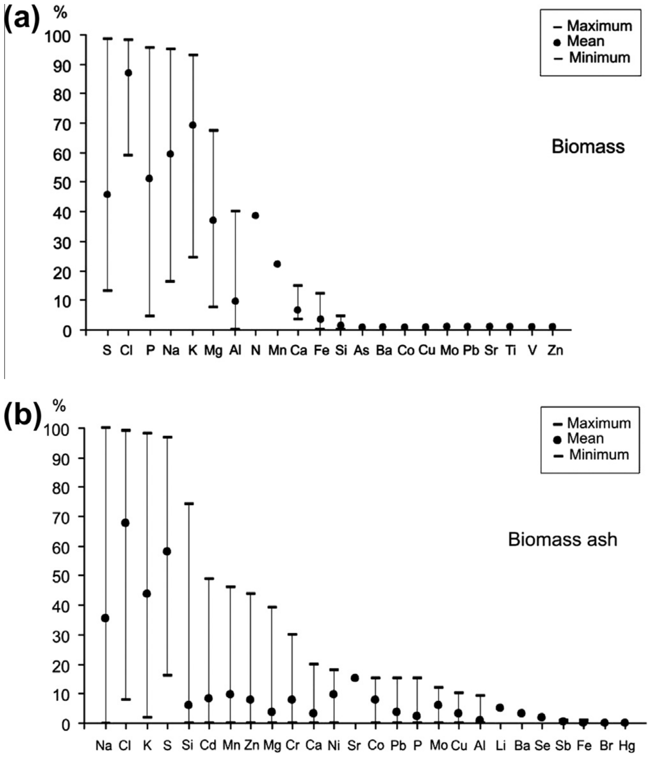

Fig. 13. Mean and range contents of water-soluble elements leached from: (a) biomass; and (b) biomass ash, wt.%.

minerals and organic phases; (2) kaolinite; (3) illite plus montmorillonite; (4) zeolites; and (5) certain organic ingredients. Such fuels can be to some extent “self-cleaning fuels” because a number of their original constituents and their newly formed products are active during fuel combustion and can play more or less a capture and immobilization role for the volatile HAP elements. Hence, the present study indicates that most of the biomass fuels could belong to these “self-cleaning fuels” group due to their: (1) enrichment in active alkaline-earth and alkaline constituents, which are characteristic of all ash types and sub-types excluding mostly “S-HA” (Figs. 1d and 2 and Tables 1, 2 and 9–18); and (2) abundance of structural organic components (cellulose, hemicellulose and lignin) in different inorganic types and sub-types, which can produce unburned chars with high specific surface area (much higher than coal) depending on composition and combustion conditions [4].

The present study shows that some biomass varieties have promising composition that could contribute significantly to the capture of volatile C, S, Cl, Hg and other trace elements in combustion residues by the subsequent inorganic and organic matter transformations in the system during biomass combustion. For example, the phase–mineral composition of BA varieties, sub-types and types evidently demonstrates the presence of such favourable minerals among carbonates, oxyhydroxides, phosphates, sulphates, chlorides and amorphous matter (Tables 10–18 and Figs. 10 and 11). On the other hand, the highly variable phase and chemical composition of biomass fuels gives the possibility of improving the performance and/or reducing of harmful emissions by modification of the feed fuel composition through tailored and self-cleaning fuel mixtures (see Sections 3.4.1.2 and 3.4.1.3). The use of such an advanced approach is of particular interest because these cleaner fuel blends may contribute to reducing or avoiding additional installations of expensive cleaning systems in power plants. For example, the reference investigations show that the high Br contents (⩾22–28 ppm) in feed fuels are effective means of oxidizing and retention of Hg in the combustion residues of power plants ([4] and references therein). The Br contents in different biomass varieties (some algae, rice straw, sugar cane trash, eucalyptus, poultry manure and certain plant ashes) are greater than the above listed and necessitate concentrations in feed fuel for power plants [4]. Hence, some Br enriched fuels could play the role of self-cleaning fuels for Hg. The presence of Br in such biomass varieties may be enough for preparation of future coal-biomass blends enriched in Br for the successful capture and immobilization of Hg. Biomass fuels enriched in Cl and particularly among “K-LA” sub-type (Figs. 1 and 2) seem to be very attractive for this purpose because the geochemical and biochemical behaviour of Br and Cl is thought to be similar [98].

It is widely accepted that biofuels as renewable energy carriers do not contribute to the greenhouse effect due to the CO$_2$ neutral conversion ([1] and references therein). However, the present study and some former data [2–4] indicate that the biomass energy can be not only carbon–neutral, but also with some extra carbon-capture and storage potential due to fixation and immobilization of CO$_2$ in the combustion residues. For example, the mineral composition of biomass ashes (produced at 500–900 °C) clearly show the intensive formation of various newly formed carbonates (Tables 11–18, Fig. 10 and [2–4]). These carbonates are a result of solid–gas reaction between the volatile CO$_2$ (released from biomass or occurring naturally in the atmosphere) and Ca, K, Mg and Na oxyhydroxides formed during biomass combustion. Such carbonates are relatively stable minerals during weathering and thermal treatment up to 900 °C [5]. Hence, the concept of “self-cleaning fuels” also is related to some extra CO$_2$ capture and storage, and observations concerning different biomass varieties and their combustion residues (ash types and sub-types) can be applied to this issue. For example, significant amounts of CO$_2$ in combustion chambers and flue emissions of biomass-fired power plants can be captured by active oxides and retained in bottom ashes and fly ashes as carbonates. Furthermore, atmospheric CO$_2$ is captured by Ca, K, Mg and Na oxides, hydroxides, sulphates, some active Ca and Ca–Mg silicates, and even pozzolanic glass in the deposited combustion residues during their storage and weathering [72]. The last two phenomena are actual extra CO$_2$ capture and storage mechanisms that can have significant importance for the combustion residues produced from some biomass fuels, namely “CK” > “C” > “K” > “S” types and particularly “CK-LA” > “C-LA” > “K-LA” > “S-MA” sub-types according to the carbonate contents in BAs (Figs. 1d, 2, 10 and 11, and Tables 10–18). It should be stated that this CO$_2$ capture-storage mechanism is much stronger for BAs than coal ashes.

3.4.2.2. Water leaching of hazardous elements from biomass ash. The reference investigations show that BAs contain significant amounts of a water-soluble fraction [15,37,45] as its content can be up to 61% [99]. Additionally, this BA fraction was classified to low (15%) medium (15–40%) and high (>40%) groups according to the amount of water-soluble K, Na, Ca and Mg oxides [37]. The reference data for water-soluble elements leached from biomass and BA are summarized in Table 21, and illustrated in Fig. 13a and b, respectively. It can be seen that the mean contents of water-soluble elements leached (in decreasing order) from various biomass varieties are: Cl > K > Na > P > S > N > Mg > Mn > Al > Ca > Fe > Si plus some As, Ba, Co, Cu, Mo, Pb, Sr, Ti, V and Zn. On the other hand, the data also reveal that these mean contents for different BAs are: Cl > S > K > Na > Sr > (Ni, Mn) > (Cd, Cr, Zn, Co) > (Si, Mo) > Li > (Mg, Pb) > (Ca, Cu, Ba) > (P, Se) > (Sb, Al) > Fe > (Br, Hg). The comparison between the above orders and data for both biomass and BA indicates that most of the ash-forming elements are prone to have higher water-soluble proportions in biomass (Al, Ca, Cl, Fe, K, Mg, N, Na, P and Ti) than in BA (S, Si). In contrast, it seems that most of the water-soluble trace elements show an opposite trend, namely greater water-soluble proportions in BA (Ba, Co, Cu, Mo, Pb, Sr and Zn, and probably Br, Cd, Cr, Hg, Li, Ni, Sb and Se) than in biomass (As, Mn and V). The above trends are a strong indication that the water-soluble nutrients are associated preferentially with biomass, while most the mobile hazardous trace elements are associated preferentially with BA. Hence, the transformation of OM in biomass (cellulose, hemicellulose, lignin, organic minerals, others) to IM in BA (inorganic amorphous matter, carbonates, silicates, oxyhydroxides, phosphates, sulphates, chlorides) induces dramatic changes in element mobility. The highly mobile trace element impurities can commonly occur in surface enriched and water-soluble salts (chlorides, sulphates, carbonates) and oxyhydroxides on the ash particles built up dominantly by water-insoluble phases. This is normally a result of intensive volatilization of many trace elements in the boilers during biomass combustion and their subsequent condensation as: (1) homogeneous nucleation; and especially (2) heterogeneous condensation with some aggregation of nucleated particles and widespread precipitation on the surface of more stable and previously formed ash particles; during cooling of flue gas emissions ([4] and references therein). It should be emphasized that this volatilization–condensation process during combustion is much more characteristic of biomass than coal [4]. The observations that most of the hazardous trace elements tend to have higher mobility in BA than in biomass give important information for the sustainable utilization of BA, especially for soil application and recovery of elements.

The present (Tables 10–18) and former [3] studies show that the water-soluble phases in BA mostly include phases of alkali and alkaline earth elements such as:

(1) Highly soluble chlorides (sylvite, halite), sulphates (arcanite, syngenite, ettringite, gypsum), oxides (lime), hydroxides (portlandite), nitrates, carbonates and bicarbonates.
(2) Certain less soluble carbonates (calcite), phosphates (phosphorites) and oxides (periclase).
(3) Some slightly soluble phosphates (apatite) and silicates (Ca silicates, feldspars).

Hence, the classification of BAs to different types and sub-types has a leading importance for their differentiation to high (commonly "K-LA", "CK-LA" and "C-LA" sub-types), medium (normally "S-MA", "C-MA", "K-MA") or less (dominantly "S-HA" sub-type) water-soluble BA categories due to occurrence of the above listed soluble minerals and insoluble silicates, glass and some oxyhydroxides and phosphates. The specified oxide associations in BAs (Fig. 2) are also indicative for the common occurrence of water-soluble components in the system. For example, the different corners of Fig. 2 may represent the preferable occurrence of: (1) less soluble minerals to the upper corner ($SiO_2 + Al_2O_3 + Fe_2O_3 + Na_2O + TiO_2$); (2) medium to highly soluble minerals to the left corner ($CaO + MgO + MnO$); and highly soluble minerals to the right corner ($K_2O + P_2O_5 + SO_3 + Cl_2O$, as N also belongs to this association).

Besides the composition of biomass [1,2] and BA [3–5], it is obvious that the combustion temperature (Tables 10–18) also has an important role in the formation of more or less water-soluble minerals in the BA system over different temperature ranges [5]. Unfortunately, the water-soluble fraction of BAs may contaminate surface and subsoil water, soil, flora and fauna (with possible subsequent penetration into the food chain) in the areas surrounding the biomass-fired power plants or BA processing facilities and disposal sites. Therefore, further detailed studies of this potentially very serious problem are required and the correlation between leaching and different BA types and sub-types could have a leading consideration for that purpose.

Finally, the chemical and mineral classifications generated (Figs. 1, 2, 8, 9 and 11) and biomass types and sub-types described, as well as major trends found (Figs. 3–7, 10, 12 and 13), offer a huge potential for future investigations and possible applications of the results. The above or similar classifications based on the combination of data from origin, composition and properties of biomass and BA can be used for the prediction of numerous issues related to innovative and sustainable utilization of biomass and BA. For example, such data have primary importance in both basic and applied aspects related to biomass and BA and can assist directly or indirectly in:

(1) Establishment of a uniform nomenclature and standards.
(2) Detection of important and combined chemical and phase–mineral associations and their application for creation of advanced and more precise specifications.
(3) Explanation or prognosis of composition and properties, as well as phase–mineral transformations and chemical interactions during thermo-chemical conversion.
(4) Characterization of formation mechanisms of solid biomass products.
(5) Identification of contaminated biomass.
(6) Adjustment of fuel blends for their ecologically cleaner and less problematic technological utilization.
(7) Specification of appropriate or potential utilization of BA, namely:
    - Bulk utilization (for soil amendment and fertilization; production of construction materials, adsorbents, ceramics and other materials; synthesis of minerals).
    - Recovery of economically valuable components and their utilization (char, water-soluble, cenosphere–plerosphere, magnetic and heavy fractions; and elements).
    - Multicomponent utilization.
    - Technological advantages and challenges (agglomeration, slagging, fouling and corrosion; low ash fusion temperatures; erosion and abrasion; co-combustion and co-gasification; others).
(8) Prediction of some environmental risks and potential health concerns related to BA (air, water, soil and plant contamination; acidity, alkalinity and leaching; volatilization, retention, capture and immobilisation of hazardous elements and compounds; ash inhalation and disposal).
(9) Prognosis and assessment of other technological, ecological and health problems or benefits such as:
    - Performance during biomass processing.
    - Novel, effective and environmentally sound thermo-chemical technologies.
    - Other appropriate or potential innovative (effective, multicomponent, wasteless), modes of sustainable biomass utilization;
    - Economically valuable or environmentally hazardous components.
    - Reduction or elimination of various environmental risks and potential health concerns such as global and local contaminations of the air, water, soil and plants by toxic and potentially toxic compounds originated from gas, liquid and solid emissions associated with biomass fuels and their conversion products.

4. Conclusions

Some conclusions based on the present overview of the ash fusion and ash formation mechanisms of biomass types and sub-types can be made:

(1) Three systematic chemical associations based on the occurrence, content and origin of elements and phases were identified and used for the inorganic matter classification of BA system, namely: (1) Si–Al–Fe–Na–Ti (mostly newly formed glass, silicates and oxyhydroxides); (2) Ca–Mg–Mn (commonly newly formed carbonates, oxyhydroxides, glass, silicates and some phosphates and sulphates); and (3) K–P–S–Cl (normally newly formed phosphates, sulphates, chlorides, glass and some silicates and carbonates). The above classification resulted in four chemical biomass ash types ("S", "C", "K" and "CK") further specified into six ash sub-types with high, medium and low acid tendencies ("S-HA", "S-MA", "C-MA", "C-LA", "K-MA" and "K-LA", as "CK-LA" sub-type is identical to "CK" type).

(2) The inorganic matter of biomass varieties has variable performance during combustion; however, the present study clearly shows that the thermal behaviour of IM, ash fusion and ash formation mechanisms of different BAs tend to be relatively: (1) diverse between the inorganic types; and (2) similar within the inorganic types and especially sub-types specified; despite some exceptions.

(3) AFTs of biomass are more variable than of coal and they are normally lower, excluding certain lignites and biomass varieties from "S" and "C" ash types. The greater concentrations of Ca, Al and Ti and lower contents of K, Si, P, S, Fe, Na and Mg (excluding some highly enriched in Si varieties) normally contribute to increased AFTs of biomass. Quite informative distributions of the DT and HT values for sub-types in low ("K-MA", "K-LA", "S-MA" and partly "CK-LA" and "S-HA"), medium (all sub-types) and high ("C-LA", "S-HA" and partly "CK-LA") temperature ranges were identified and such distributions are applicable for some preliminary and proximate DT and HT prediction purposes of BAs.

(4) The common ash fusion mechanisms for BA sub-types normally include:
    - Lower AFTs with short ("S-MA") or large ("K-MA" and "K-LA") softening–melting ranges and slow ("K-MA"), medium ("K-LA") or high ("S-MA") flow-dissolution rates.
    - Medium AFTs with short softening–melting range and high flow-dissolution rate ("C-MA").
    - Higher AFTs with moderate softening–melting range ("S-HA" and "C-LA") and medium ("S-HA") or high ("C-LA") flow-dissolution rates
    - Different AFTs with moderate softening–melting range and medium flow-dissolution rate ("CK-LA").

(5) The common ash formation mechanisms of BA types and sub-types can be characterized as:
    - Sequential phase–mineral transformations including: (1) initial formation of intermediate and less stable chlorides ("S" and K"), hydroxides ("C", "K" and "CK"), carbonates (all types), sulphates ("S", "K" and "CK"), phosphates ("C") and inorganic amorphous material (all types); (2) subsequent generation of more stable silicates (all types), phosphates ("C", "K" and "CK") and oxides ("C", "K" and "CK"); and then (3) softening and melting ("S", "C" "K", "CK" and especially "S-HA") accompanied by dissolution of the refractory minerals ("S", "C" "K" and particularly "S-MA") by less ("S", "C", "K" and especially "S-HA"), medium ("CK") or more active ("S", "C", "K" and particularly "S-MA) melts; with increasing combustion temperatures in the system.
    - Final crystallization of the silicates in melt (all types) and formation of glass (all types) accompanied by limited ("S"), significant ("C") or extensive ("K" and "CK") salt condensation, and limited ("S") or intensive ("C", "K" and "CK") hydroxylation, hydration and carbonation of newly formed phases during cooling of BA.
    - Some limited ("S") or extensive ("C", "K" and "CK") post-combustion transformations of the newly formed minerals and phases to stable species during weathering (tertiary) among hydroxides and carbonates due to their hydration, hydroxylation and carbonation by moisture and CO_2 in the air through storage of BA.

(6) Numerous simple or more complex indexes based on chemical composition of BA are used for predicting the ash fusion, slagging, deposit formation, fouling, agglomeration, sintering or corrosion problems during thermo-chemical conversion of biomass. The present study shows that such chemical indexes can be only preliminary and proximate indicators for such problems because the real behaviour for a biomass fuel during combustion is directly related to the phase–mineral composition and ash formation mechanism of this specific fuel through processing. The chemical approach alone cannot adequately predict or explain the real behaviour of biomass fuels and their conversion products because the leading reasons for the above problems are modes of element occurrence (specific phases and minerals that contain this element) in the system and their behaviour during combustion. Therefore, the assignment of biomass varieties to combined chemical and mineral ash types and sub-types can supply much better information for the prediction and evaluation of the above problems than chemical indexes.

(7) The lower AFTs with short softening–melting range and high flow-dissolution rate ("S-MA") seem to be the worst case for slagging and fouling. In contrast, higher AFTs with moderate softening–melting range ("S-HA" and "C-LA") and medium ("S-HA") or high ("C-LA") flow-dissolution rates are the best cases for avoiding such problems.

(8) Favourable and less problematic future co-combustion can include mixtures between biomass, coal and other solid fuels with an adjustment of chemical composition for fuel blends to fit preferentially closer to "C-LA" and "S-HA" sub-types and some areas of "S-MA", "K-MA", "K-LA" and "CK-LA" sub-types.

(9) A phase–mineral classification based on the contents of amorphous matter (normally pozzolanic phases), silicates (commonly inert minerals) and other phases (mostly active minerals) was created for the prediction of potential innovative utilization of BAs. It was found that BAs can exhibit preferably: (1) inert (normally "S-HA"); (2) pozzolanic (commonly "C-MA", "S-MA" and "K-MA"); and (3) active or cementitious (mainly "C-LA", "CK-LA" and K-LA) binding properties.

(10) The study of the volatilization and capture of hazardous elements during biomass combustion shows that:
    - The mean contents of elements such as Hg > (Cd, Sb, Se, V) > Br > Cr > Pb > Zn > Cl > As > S > K > Na demonstrate the highest volatilization potential during biomass combustion and these volatilized elements present some environmental risk and potential health concern.
    - The volatilization behaviour decreases in the order: "K" > "C" > "CK" > "S" for BA types. Biomass normally with: (1) low ash yield and less acid and detrital tendencies; and (2) high authigenic mineralization; is more prone to such volatilization (particularly "K-LA", "C-LA" and "CK-LA"). In contrast, more limited loss of volatile elements could be expected when they mainly occur in stable minerals in biomass such as silicates, oxides and

some phosphates ("S-MA", "C-MA", "K-MA" and especially "S-HA") and these elements should remain in the combustion residues.
- Increased capture of volatile elements in combustion residue can be caused by some minerals or phases with well-known sorbent properties and present as carbonates, oxyhydroxides, phosphates, sulphates, chlorides and amorphous matter in the combustion residue (especially "C-LA", "CK-LA" and "K-LA").
- Most of the biomass fuels could belong to the "self-cleaning fuels" group due to their enrichment in active alkaline-earth and alkaline constituents, which are characteristic of all ash types and sub-types excluding mostly "S-HA".
- There is an extra CO_2 capture and storage for the combustion residues produced from some biomass fuels, namely "CK" > "C" > "K" > "S" types (particularly "CK-LA", "C-LA" and "K-LA" sub-types) because significant amounts of CO_2 can be captured by active oxides and retained in the ashes as carbonates.

(11) The investigation of the water leaching of hazardous elements from biomass ash reveals that:
- BAs contain significant amounts of a water-soluble fraction with some utilization potential and/or environmental risk and health concern.
- The mean contents of water-soluble elements leached from: biomass are Cl > K > Na > P > S > N > Mg > Mn > Al > Ca > Fe > Si plus some As, Ba, Co, Cu, Mo, Pb, Sr, Ti, V and Zn; while these elements for BAs are Cl > S > K > Na > Sr > (Ni, Mn) > (Cd, Cr, Zn, Co) > (Si, Mo) > Li > (Mg, Pb) > (Ca, Cu, Ba) > (P, Se) > (Sb, Al) > Fe > (Br, Hg). It is indicated that the water-soluble nutrients are associated preferentially with biomass, while most the mobile hazardous trace elements are associated preferentially with BA.
- The specification of BAs to different types and sub-types has a leading importance for their differentiation to high (commonly "K-LA", "CK-LA" and "C-LA" sub-types), medium (normally "S-MA", "C-MA", "K-MA") or less (dominantly "S-HA" sub-type) water-soluble BA categories due to occurrence of soluble chlorides, sulphates, oxyhydroxides, nitrates, carbonates and phosphates, and insoluble silicates, glass and some oxyhydroxides and phosphates.

(12) The definitive utilization, technological and environmental advantages and challenges related to biomass and BA associate preferentially with their specific types and sub-types and they could be predictable to some extent by using the above or similar combined chemical and phase–mineral classification approaches.

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